IMPERIAL INSTITUTE

MONOGRAPHS ON MINERAL RESOURCES
WITH SPECIAL REFERENCE TO THE
BRITISH EMPIRE

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PREPARED UNDER THE DIRECTION OF THE
MINERAL RESOURCES COMMITTEE OF THE
IMPERIAL INSTITUTE

VANADIUM ORES

BY
MEMBERS OF THE SCIENTIFIC AND TECHNICAL STAFF
OF THE IMPERIAL INSTITUTE

WITH A MAP

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IMPERIAL INSTITUTE

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GENERAL PREFACE

THE Mineral Resources Committee of the Imperial Institute has arranged for the issue of this series of Monographs on Mineral Resources in amplification and extension of those which have appeared in the *Bulletin of the Imperial Institute* during the past fifteen years.

The Monographs are prepared either by members of the Scientific and Technical Staff of the Imperial Institute, or by external contributors, to whom have been available the statistical and other special information relating to mineral resources collected and arranged at the Imperial Institute.

The object of these Monographs is to give a general account of the occurrences and commercial utilization of the more important minerals, particularly in the British Empire. No attempt has been made to give details of mining or metallurgical processes.

HARCOURT,
Chairman, Mineral Resources Committee.

Imperial Institute, London, S.W.7.
July 1920.

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NOTE: *Numerals in square brackets in the Text refer to the Bibliography at the end.*

VANADIUM ORES

CHAPTER I

VANADIUM ORES: THEIR OCCURRENCE, CHARACTERS AND USES

INTRODUCTION

VANADIUM was discovered in the year 1801 by Del Rio, then Professor of Mineralogy at the School of Mines, Mexico City, in lead ore from Zimapan in the State of Hidalgo, and was named by him " erythronium " from the property possessed by its salts of becoming red when heated with acids. In 1805 a French chemist, Collet-Descostils, announced that Del Rio's erythronium was impure chromium, and this statement was accepted by the discoverer. In 1830 Sefström found what he took to be a hitherto unrecognized metal in the iron ores of Taberg in Småland, Sweden, which he called " vanadium " from Vanadis, a cognomen of the Scandinavian goddess Freia. This metal was shown to be identical with Del Rio's erythronium by Wöhler, who proved that the Zimapan ore was a lead vanadate. In 1831 Berzelius published a description of its compounds, but the chemistry of the metal was not thoroughly worked out till the classic work of Roscoe was completed more than 30 years later [1], [2].

Pure metallic vanadium was first prepared in 1904 on a very small scale by Weiss and Aichel, who reduced oxides of vanadium with *mischmetal* (metals of the cerium and yttrium group) and obtained a white regulus, which exhibited facets of rhombohedral crystals agreeing with those of

arsenic, antimony and bismuth in habit, a result to be expected from the position of vanadium in the periodic table. Of previous results made in attempting to obtain the pure metal Roscoe's silvery-white powder, first produced in 1867 in reducing the chloride (VCl_2) by hydrogen, always contained some hydrogen, and Moisson's electric furnace product contained carbon, while Roscoe showed that Berzelius's vanadium was either an oxide or a nitride. The pure substance is a white, lustrous metal, harder than quartz, non-magnetic, and with a melting point of about 1680° C. It oxidizes slowly in the air at ordinary temperatures, but more rapidly when heated, going through various degrees of oxidation, and showing a characteristic colour for each oxide—brown (V_2O), grey (V_2O_2), black (V_2O_3), blue (V_2O_4), and red (V_2O_5) [3]. It is unattacked by hydrochloric or hydrobromic acids, cold sulphuric acid or cold caustic alkalies; however, it dissolves readily in hot sulphuric acid and caustic potash, and easily forms green solutions with nitric acid and aqua regia. It forms alloys with iron, nickel, cobalt, copper, aluminium, tin, platinum and other metals, and also forms compounds with silicon, phosphorus, nitrogen, carbon and, possibly, hydrogen. The chemistry of the element is very complex and cannot be discussed here.

Vanadium Minerals

The principal ores of vanadium, placed in order of abundance, are *patronite, roscoelite, carnotite* and *vanadinite*. Patronite is a sulphide of vanadium. Roscoelite is a silicate, and is usually regarded as a muscovite in which vanadium has partly replaced aluminium. Carnotite is a uranyl-potassium vanadate, which is mined chiefly for its radium content, uranium and vanadium being obtained as by-products. Vanadinite is a chloro-vanadate of lead.

Other minerals, which have been, or are being, mined in one or two localities on a much smaller scale than the above ores, are: *Tyuyamunite*, uranyl-calcium vanadate, allied

to and sometimes associated with carnotite; *descloizite*, a vanadate of lead and zinc; *cuprodescloizite* (or *ramirite*), and *dechenite*, which are varieties of descloizite; *mottramite*, *chileite* and *psittacinite*, vanadates of lead and copper; *endlichite*, allied to vanadinite; *brackebuschite*, a vanadate of lead, iron, manganese, etc.; *turanite*, a copper vanadate; *uvanite*, a hydrous uranium vanadate; and *kentsmithite*, a sulphate of vanadium.

Among the rare minerals of vanadium are: *Pucherite*, a vanadate of bismuth; *hewettite*, *metahewettite*, *pascoite*, *fernandinite* and *minasragrite*, hydrous calcium vanadates, or other alteration products of patronite; and *pintadoite*, a hydrous calcium vanadate occurring in the carnotite plateau region of Colorado, United States.

Among vanadium minerals of complex and somewhat doubtful composition are: *Ardennite*, a vanado-silicate of aluminium and manganese with some arsenic; *volborthite* and *calciovolborthite*, hydrous vanadates of copper, barium and calcium; and *sulvanite*, a sulpho-vanadate of copper [4], [5].

Occurrences of Vanadium

For a long time after its discovery vanadium was thought to be very rare, but it has more recently been found in small quantities in many rocks, and even in the ashes of plants, and is now known to be one of the more abundant minor constituents of the earth's crust. F. W. Clarke [5/p. 33], in computing the average composition for the whole of the earth's crust, takes into account 102 analyses of igneous rocks in which vanadium has been determined, and from these he deduces that it is present in the igneous rocks to the extent of 0·026% vanadium trioxide (V_2O_3). The element seems to be less common in sedimentary rocks, so that it forms a somewhat smaller proportion of the crust as a whole, but, nevertheless, it exceeds in amount many of the metals such as lead and copper, which are usually regarded as common. Of course, in these computations

what are usually referred to as " ore-bodies " have not been taken into account, but as such are in exceedingly small amount in relationship to the main rock masses, they are almost negligible in this respect.

In the igneous rocks few instances are recorded of remarkable quantities of vanadium in those of an acid composition, and it is found, more particularly, in the intermediate and basic magmas, especially the latter, as will be seen below. In the sediments the metal is usually found associated with elements such as iron and aluminium, whose oxides, in common with those of vanadium, are precipitated from alkaline solution; or in association with fossil wood, where the wood may be the direct source of the vanadium or merely the precipitant. It occurs therefore in such rocks as the red clays and terrigenous muds of the deep oceans, the residual bauxites and laterites, coal ashes and highly ferruginous beds, such as those of the " minette " ores of Lorraine and Luxemburg.

The occurrences cited above, though serving to show that vanadium has a very wide distribution in the earth's crust, are, nevertheless, of very little economic importance, and for the commercial sources of the metal we must turn to more specialized and concentrated deposits. Taking account of these, the sources of vanadium compounds which are of present or potential economic value fall into several major divisions. A classification of these occurrences was proposed by De Launay [6/p. 723] in his *Gîtes Minéraux et Métallifères*; this was in the main built on a genetic basis, and with certain modifications is adopted here:

I. *Segregations from basic magmas.*—Vanadium is found in stony (non-metallic) meteorites, though not in meteoric irons; in association with ilmenites and titaniferous magnetites such as those of Taberg in Småland, and in the Adirondacks; also in chromite and other similar ores, and with the rutile of apatite-bearing pegmatites.

II. *In veins of hydrothermal origin* (generally associated with acid igneous intrusions).—In these vanadium is asso-

ciated with either uranium as at Joachimsthal in Bohemia (Czechoslovakia), or with gold tellurides, as in the gold lodes of Boulder Co., Colorado, and of Kalgoorlie. In the first instance quoted the uranium occurs in an uncertain state of combination in pitchblende as well as in red dolomite, associated with the pitchblende, the mineral association being very like that of the Colorado carnotites, and showing similar surface alteration. An ore of origin intermediate between these two types seems to be the vanadinite of the gold-bearing silver-lead veins in the Province of San Luis in Argentina, described by Bodenbender. These veins contain a certain proportion of molybdenum, and are in close association with wolframite-bearing pegmatites, as is the case with the Colorado gold-quartz veins. In this division may also be included the roscoelite-bearing sandstones of Placerville and Vanadium (Newmire) in Colorado, the mottramite of Mottram St. Andrew in Cheshire, the vanadium associated with the native copper of the Lake Superior region, and the carnotite of Radium Hill and Mt. Painter in South Australia. These deposits, though of widely different types, were all presumably deposited from warm solutions rising along fault-planes and shatter-belts.

III. *Sulphide ores associated with hydrocarbons.*—In this class may be placed the patronite deposit of Minasragra, Peru, the so-called " coal veins " (asphaltites), also of Peru, and the asphaltites of Oklahoma, Nevada and elsewhere. The vanadium is probably present in the form of patronite or some other sulphide, which appears to have been introduced in solution in the hydrocarbons of the asphaltite, and in some instances, as at Minasragra, to have separated from solution after the intrusion took place. Vanadium sulphide is found to be soluble in asphaltite, and can be prepared by acting on an oxide with the vapour of carbon disulphide. It now seems to be generally agreed that the asphaltites (*see* p. 57) are the residuary material from the seepage of petroleum deposits, so that the necessary conditions for the formation of this class of ores are: (1) Vanadium

as oxide, disseminated through a fairly porous rock; (2) impregnation with a hydrocarbon to a greater or less degree; (3) a source of sulphur or sulphuretted hydrogen. Hence these deposits are found either filling fault-planes or fissures in compact rocks in regions where petroleum deposits have existed in the neighbourhood of volcanoes, and these conditions are fulfilled both in Peru and in Oklahoma.

IV. *The oxidized upper levels of lead and copper lodes.*—In these deposits the vanadium minerals all belong to the vanadate class (vanadinite, descloizite, chileite, etc.), and are found with oxidized lead, zinc and copper minerals, pyromorphite, mimetite, wulfenite, stolzite, hopeite, etc. They are known in many places, for example, in Wanlockhead and Leadhills in Scotland; Northern Rhodesia; Spain; the South-Western United States; Mexico; and Russian Turkestan. The vanadium minerals are confined to the oxidized zone, and are usually richest just above the level of ground water, where they occur generally lining cavities and fissures in the gossan. Only small amounts of vanadium may be found below and close to the level of ground water. The origin of the vanadium compounds in these deposits is a matter for some speculation. No vanadium is usually detectable in the unoxidized ore, and the general form of the occurrences seems to point to some "external source" for the metal, though what this may be is so far unknown.

V. *Deposits in sedimentary rocks.*—The minerals of these deposits are entirely oxidized compounds, and are as a rule associated with iron, aluminium, copper, lead, zinc, cobalt and carbonaceous matter. In this division fall the carnotite deposits of Colorado and Utah; the French bauxites and laterites; the minette ores of Lorraine and Luxemburg; the shales and clays and coal ashes of New South Wales and other places; the coal ashes of San Rafael, Argentina; and many other similar occurrences of little or no importance.

At this point it is worth while to notice how the vanadium is associated with copper, lead, zinc and cobalt, in the sediments just as much as in the oxidized gossans, though

in the gossans it is generally accompanied by carbonaceous matter, as is the case with the copper shale of Mansfeld, Germany, and the grits of Voskresensk in the Ural Mts.

METALLURGY OF VANADIUM

Metallurgically the ores of vanadium may be divided into four classes [1]: (1) *Sulphides, e.g.* patronite; (2) *silicates, e.g.* roscoelite; (3) *uranium-vanadium ores, e.g.* carnotite; and (4) *metallic vanadates, e.g.* vanadinite, descloizite and volborthite. Each class of ore requires a different preliminary treatment:

(1) Patronite was originally treated by a wet extraction method, but a dry method is now used. The ore and necessary fluxes are subjected to matte-smelting in a reverberatory furnace. The heavy metals go into the matte, and the vanadium and gangue material into the slag. The slag is granulated in water, dried, and reduced to ferro-vanadium in a shaft furnace [7].

(2) Roscoelite is roasted with salt and pyrite. The product is leached with hot water in vats, the vanadium going into solution as sodium vanadate. When cold, ferrous sulphate is added to the solution, vanadium being precipitated as iron vanadate [8], [9].

(3) In the case of carnotite, radium is first extracted from it, the vanadium being recovered as a by-product. Several methods have been devised for the extraction of the radium, but some of these are only applicable to selected ores. The method recommended by the United States Bureau of Mines [10] consists in first leaching the ore with strong nitric acid, brought to the temperature of 100° C. by steam. The solution containing the metals is then neutralized with sodium hydroxide, and barium chloride and sulphuric acid are added in order to precipitate the radium as radium-barium sulphate. The precipitate settles in three or four days, after which time the clear liquid

[1] Communication from Mr. J. Kent Smith.

is decanted into tanks, and is treated with an excess of boiling sodium carbonate solution, whereby the iron, calcium and most of the aluminium are precipitated. The solution now contains sodium-uranyl carbonate and sodium vanadate. It is nearly neutralized with nitric acid, and sodium hydroxide is added to precipitate the uranium as sodium uranate. The remaining solution is neutralized with nitric acid, and ferrous sulphate is added, when the vanadium is precipitated as iron vanadate. By this process it is claimed that 90% of the radium is recovered, nearly all the uranium, and 50% of the vanadium.

(4) The vanadates of lead, copper and zinc are generally fused with sodium salt; the lead, copper or zinc separates as metal, and the vanadium goes into the slag as sodium vanadate. If the resulting slag is too low-grade for direct reduction to ferro-vanadium, it can be crushed, mixed with sulphuric acid, baked to a dry cake, crushed again and boiled with water for several hours. The vanadium goes into solution as vanadium sulphate, which is subsequently roasted and reduced to ferro-vanadium by the thermit process [11].

Experimental tests, being modifications of the above process, on vanadinite [12] and cupro-descloizite [13] are described by Conley.

Ferro-vanadium.—In order to produce ferro-vanadium the vanadium must be in the form of vanadic oxide or of iron vanadate. In a modification of the thermit process the crushed material, mixed with aluminium shot as the reducing agent and the necessary amount of iron scale or turnings and fluxes, is treated in a gas-fired open-hearth furnace, or in a magnesite-lined iron crucible, previously heated to redness. The reaction takes place according to the following equation:

$$3V_2O_5 + 10Al = 6V + 5Al_2O_3.$$

With a vertical shaft furnace a much higher temperature (from 2500° to 2800° C.) and a much larger output can be obtained than with a crucible. A furnace 9 ft. 3 in.

high and 4 ft. 6 in. wide will produce 125,000 lb. of alloy in one run.

With the electric furnace silicon or ferro-silicon is used as the reducing agent. The furnace, lined with magnesite, is charged with steel turnings. When these are melted, vanadic oxide is added and is followed by a mixture of silicon and lime. When the slag is fluid, which takes from 1 to 1½ hours, it is raked off, and more vanadic oxide is added; this is followed by a mixture of silicon and lime. After another hour the slag is again raked off and the metal is tapped. The reactions are expressed by the following equations:

$$2V_2O_5 + 5Si = 4V + 5SiO_2;$$
$$5SiO_2 + 5CaO = 5CaSiO_3.$$

The slag usually contains less than 1% vanadium, and the alloy contains 30% vanadium; 4 to 8% silicon; 0·5% carbon; 0·05% sulphur; and 0·05% phosphorus [14/p. 730], [8].

Electric furnace methods using carbon as a reducing agent have long been looked upon with disfavour, but, in recent years, the Vanadium Corporation of America appears to have succeeded with the use of carbon where others have failed. With carbon a very high temperature zone must be produced inside the reducing mass, preferably near the top of the metal bath. A rectangular three-phase furnace with a water-cooled cover and water-cooled bushings for three 12 in. graphite electrodes is used. The mixture of ore, coke and fluxes is ground fine and thoroughly mixed, and is fed into the furnace by automatic feeders through water-cooled bushings in the top of the furnace. The furnace is tapped at intervals of 6 hours, approximately, for metal and slag.

Aluminium-vanadium.—To produce this alloy, fluorspar is first melted in the electric furnace. Scrap aluminium is then dropped into the bath of fluorspar as fast as it can be charged without allowing arching on the aluminium. As soon as all the aluminium is charged, a thermit mixture of vanadic oxide and aluminium shot is added.

Cupro-vanadium.—For the manufacture of this alloy a mixture of vanadic oxide, copper oxide, aluminium shot, lime, soda ash and fluorspar is made, and about 10 lb. of the mixture is charged at first into a magnesite-lined crucible. An ounce or two of the mixture is added to a small amount of sodium peroxide on a large piece of paper, and the whole is placed in the crucible on the top of the charge and ignited. The reaction takes place violently. As soon as it has apparently stopped, the rest of the charge is added in about 2 or 3 lb. lots. The slag is removed by skimming or tapping, and the alloy is tapped into an iron mould [14/pp. 731–2].

USES OF VANADIUM

For some time after its discovery vanadium remained a chemical curiosity, but the announcement in the early sixties of its use in certain dyeing processes caused a search to be made for the element, and small quantities were produced for some years from the Joachimsthal deposits in Bohemia and from the iron slags of Le Creusôt in France. At this time it found a use in the transformation of indigotine into indigo; in the preparation of various shades of aniline dyes; as a catalyst in the oxidation of aniline hydrochloride to a fixed black, which found considerable use as an indelible ink; as a mordant in the transformation of the cellulose of vegetable fibres to oxycellulose; in the gilding of pottery; as a photographic developer and sensitizer [1/p. 45], and even in medicine [15]. Of these uses the two chief were the manufacture of aniline black for indelible ink, and as a mordant; the latter method of employment was, however, soon superseded owing to the deleterious effect on the fabric.

The most important use, however, is in its addition to steel or non-ferrous metals as a constituent of certain alloys, such as ferro-vanadium, cupro-vanadium and aluminium-vanadium. The quantities added are very small, and the part played by the vanadium in determining the properties of the vanadized metals perhaps requires further

critical study, but the effect in every instance seems to be the toughening of the metal and the increase of its power of resistance to repeated shocks or varying stresses. By far the most important of these alloys is of course ferro-vanadium, and it is for the manufacture of this alloy that most of the vanadium ores produced are used. In a vanadium steel the amount of vanadium present is very small, usually only about 0·25%, as it is found that the properties of the steel are not altered perceptibly by further additions. Vanadium is, however, added in rather larger amount to the molten steel since, owing to the readiness with which it takes up oxygen and nitrogen, some of it finds its way into the slag.

The behaviour of vanadium in steel has been described as follows by J. Kent Smith in discussing a paper by McWilliam and Barnes [16]:

(1) Vanadium is a scavenger and removes both oxides and nitrides, leaving the metal indirectly toughened and in the best condition to receive further treatment;

(2) A portion of the vanadium goes into solid solution under normal conditions in the ferrite portion of the steel —the ferrite of vanadium steel is much more resistant to wear and to the formation of slip bands than ordinary ferrite. Also, as it tends to oppose the ready passage of carbides through the metal, its effect is to produce a steel of marked sorbitic structure;

(3) The strengthening seems to be due partly to the formation of complex carbides, especially susceptible to improvement by tempering.

According to G. L. Norris [17], only a few hundredths of 1% of the vanadium combines with the ferrite. This minute amount, however, appears to increase the strength, toughness, hardness and resistance to abrasion of the ferrite. Nearly all the vanadium, however, is found in the pearlite, in chemical combination with the cementite, as a compound carbide of vanadium and iron in the case

of ternary steel, and as more complex carbides in the case of quaternary steel. According to Norris, the beneficial effects of vanadium in steel are not due to its removal of minute quantities of oxygen and nitrogen from the steel. In other words, it does not act as a scavenger, and its value for this purpose is negligible. The vanadium occurs in a granular or sorbitic condition in the pearlite—doubtless one of the reasons for the mechanical superiority of steel, containing vanadium, not only statically, but dynamically. The effect of vanadium on the physical or mechanical properties of steel increases with the percentage of vanadium until about 1% is present, after which there is a decrease. With over 3% the steel is actually softened, even after quenching.

Steel containing vanadium is in demand for the following:

(1) *Wrought steel.*—Piston rods, crank shafts, tyres, springs, cutter punch and die steel, rock drills, saw edge tools, high-speed tool steel (where the addition of 1% vanadium is said to reduce the necessary quantity of tungsten considerably), armour plate, gun shields, gun tubes, torpedo tubes.

(2) *Steel castings.*—Locomotive frames, draw bars, cross-heads, motor car parts, aeroplane parts, etc.

(3) *Cast iron.*—Railway wheels, cylinders, etc.

According to J. Donaldson, vanadium increases the tensile, transverse and compressive strengths of cast iron, owing to the effect it has on the carbon in assisting to retain it in the combined form [18]. Previous experiments by W. H. Hatfield also showed that the presence of vanadium in the carbide renders the latter more stable [19].

Standard ferro-vanadium contains between 30 and 40% vanadium, less than 0·5% carbon, about 2% aluminium, less than 0·1% sulphur, and less than 0·1% phosphorus. It has a fine fracture and is silvery in colour. The following are analyses of some vanadium alloys:

Analyses of Various Vanadium Alloys

—	Ferro-vanadium [20].			Aluminium-vanadium [14].	Cupro-vanadium [14].
	A	B	C		
Vanadium	46·20	30·90	37·50	15·00	8·40
Iron	50·30	66·25	59·40	1·00	1·10
Aluminium	1·27	0·16	0·80	76·37	22·30
Manganese	trace	0·06	0·50	—	—
Silicon	1·03	0·34	1·00	3·76	0·70
Carbon	0·03	1·58	0·15	0·61	0·10
Sulphur	0·05	0·03	0·15	—	—
Phosphorus	0·02	0·07	0·25	—	—
Arsenic	0·18	0·36	0·25	—	—
Copper	0·05	0·09	—	—	66·15
Nickel	0·81	—	—	—	—

Note.—A and C were made by aluminium reduction; B by reduction in the electric furnace (*see* p. 9).

World's Production of Vanadium

Up to the beginning of the present century the production of vanadium ores was very small. From about 1860 onwards a small output had been maintained from Joachimsthal in Bohemia and from the Creusôt slags, and later from Spain and Mexico, but it was not until the discovery of the Peruvian ores of Minasragra in 1904 that any great development was made in the use of the metal. These last deposits are practically at present the sole source of the world's supply, though considerable quantities can be obtained if required from Colorado and Utah, United States.

On the following page is a summary of the world's recent production.

Additional small productions not included in the table on p. 14, which have been exported from various countries at different times, will be given later in the monograph.

Producing Companies.—Several companies have at various times made some output of vanadium ores and of ferro-vanadium, but mostly on rather a small scale. In 1915 the principal producers were the American Vanadium

World's Production of Vanadium

(Metric tons)

—	Peru.[1]		United States.[2]	Argentina.	Spain.
	Concentrate.	Metal in Concentrate.	Metal.	Concentrate.	Concentrate.
1909 . .	1,749	392	*	*	*
1910 . .	3,130	702	*	*	*
1911 . .	2,249	505	*	14	199
1912 . .	3,048	684	300	40	38
1913 . .	none	none	392	none	none
1914 . .	15	3·5	452	*	*
1915 . .	3,145	804	569	*	*
1916 . .	3,448	773	417	*	*
1917 . .	4,083	819	439	*	*
1918 . .	2,184	371	250	*	*
1919 . .	2,947	502	224	*	*
1920 . .	9,700 [3]	1,110 [4]	462	*	*
1921 . .	918 [5]	469 [5]	183 [5]	*	*
1922 . .	none	none	100 [4]	*	*

[1] *Bol. Cuerpo. de Ing. de Min. del Peru.*
[2] Letter from Director, *U.S. Geol. Survey.*
[3] *British Cons. Rept.*, Oct. 31, 1921.
[4] Estimated.
[5] *Min. Res.* Pt. 1, *U.S. Geol. Survey.*
* Information lacking.

Co. of Bridgeville, Pennsylvania, which operated the mines of Minasragra, Peru; the Primos Chemical Co., which worked the roscoelite deposits of Vanadium (Newmire) in Colorado, and, to a less extent, the Standard Chemical Co., which produced vanadium as a by-product in the extraction of radium from carnotite ores in the Paradox Valley district of Colorado. Of these the first mentioned was by far the most important, as will be seen below.

In September 1920 the interests of the American Vanadium Co. and of the Primos Chemical Co. were united in the Vanadium Corporation of America, which now controls practically the whole of the world's supply of available vanadium ores. This new company has closed down the roscoelite workings in Colorado, and therefore, with the exception of the small amount derived from carnotite,

all vanadium at present produced comes from Peru. Figures as to the total output and prices of ferro-vanadium alloy have been kindly furnished by Mr. B. D. Saklatwalla, the General Superintendent of the Vanadium Corporation of America, and by the United States Geological Survey. The former estimates that during the years 1912 to 1920 approximately 26,700,000 lb. of ferro-vanadium alloy were produced from the Peruvian patronite ores. During the same period 2,900,000 lb. of alloy were provided by the roscoelite deposits of Colorado.

The output from carnotite ores is more difficult to determine since the production comes from a number of small sources, but it appears that between 350,000 and 450,000 lb. of ferro-vanadium have been obtained from these ores in the eight-year period mentioned above. The vanadium content of the ferro-vanadium from all these sources has varied between 32 and 41%.

With regard to prices, Mr. Saklatwalla writes as follows: " As to the price of ferro-vanadium, this has fluctuated quite considerably within the eight or ten years. At the beginning of the industry around 1909–10 the average price had been about $5·00 per pound of contained vanadium (in ferro-vanadium). This price during 1915–16 was down to about $2·50 per pound of contained vanadium, and since then it has successively risen to as high as $6·00 or $7·00 per pound of contained vanadium during the year 1920. At present (September 1921) the price has again been lowered to approximately $5·00 to $5·50 per pound of contained vanadium.

" The reason of the lower price during 1916 was the fact that the ferro-vanadium at that time was manufactured from ore running high in vanadium percentage. This percentage was continually decreased in the ore, making the cost per pound of contained ' V ' in the ore higher, and also owing to the very much increased cost of water transportation during the period of the war, naturally, the price of the finished alloy had to be increased. The present curtailment in price has been due to the fact that within

the last year or two transportation in Peru from the mines to the sea coast has been considerably improved, owing to the Vanadium Corporation of America building a railroad from the mines to the connecting point on the Peruvian Central Railroad (the portion of the railroad from Lake Punrun to Ricran is not yet finished). This transportation was done by means of llamas in the previous years.

"Also the Vanadium Corporation of America has put up a hydro-electric power plant at the mines for conducting their operations, whereas formerly all operations were carried out by hand. You will see from these statements the justification of the price fluctuations."

According to the United States Geological Survey, the prices are as follow:

Prices of Metallic Vanadium in Ferro-Vanadium in the United States

—	$ per lb.	—	$ per lb.
1912 . .	2·00–5·00	1918 . .	5·50–8·50
1913 . .	1·80–2·50	1919 . .	5·50–8·50
1914 . .	1·80–2·50	1920 . .	3·00–8·50
1915 . .	1·80–2·50	1921 . .	4·25–7·00
1916 . .	1·80–2·50	1922 . .	3·00–4·50
1917 . .	2·50–5·50		

According to the Survey in the year 1920, eight manufacturers in the United States produced 2,290 gross tons of ferro-vanadium, containing on the average 32·4% vanadium and valued at $9,074,048. All this alloy was sold in the country, and 4 tons was imported, so that though no figures are available the American output of vanadium steel was considerable.

CHAPTER II

SOURCES OF SUPPLY OF VANADIUM ORES

(*a*) BRITISH EMPIRE

EUROPE

Great Britain

Vanadiferous minerals have been reported from a number of places in Great Britain, but unfortunately they exist nowhere in payable quantities.

The most important of the occurrences are those of Mottram St. Andrew and Alderley Edge in Cheshire [21], in which the mineral mottramite was originally discovered and later described by Roscoe [22]. At Alderley Edge the basement bed of the Keuper series takes the form of a conglomerate, which cropping out with a westerly dip, forms a prominent escarpment or " edge " facing the east. Just on the north side of the village an east and west fault with a downthrow to the north shifts the outcrop of this conglomerate, about two miles to the east, to Mottram St. Andrew. On both the north and south sides of this fault, *i.e.* at Mottram St. Andrew and at Alderley Edge respectively, the cementing material of the conglomerate and the sandstone overlying it for some way is found to have been replaced in a somewhat irregular manner by ores of copper, lead, cobalt and other metals, with which is associated some vanadium. The copper occurs generally in the form of either malachite or azurite, the lead partly as galena, but for the most part as cerussite, the cobalt in the form of a black earthy oxide, while the vanadium is sometimes present as vanadinite associated with pyromorphite, but,

more commonly, as the basic lead-copper vanadate, mottramite. The mottramite generally coats the sandstone as incrustations, which may be composed of very minute crystals or of apparently amorphous material. These incrustations are for the most part very thin, but in places they attain a thickness of $\frac{1}{10}$ to $\frac{1}{13}$ in., while occasionally pieces as large as a walnut have been found.

These mines were worked for copper prior to the year 1877, and again during the war, but have never been used as a source of vanadium. Similar lead-copper-cobalt deposits are found scattered about in the Triassic rocks of Staffordshire, Cheshire and Shropshire, always associated with faults, but vanadium does not seem to have been specifically recorded from any of them [21], [23 to 25]. In addition to the occurrence in Cheshire, vanadinite has been discovered in small quantities associated with pyromorphite at Leadhills and at Wanlockhead [26].

It is also frequently noticed that refractory goods manufactured from the clays of the Stourbridge district often show a yellow efflorescence due to the presence of a small quantity of vanadium, as do bricks made from some of the clays of New South Wales (*see* p. 23). None of these occurrences, however, is of any value.

AFRICA

Northern Rhodesia

Vanadium minerals are found associated with the oxidized lead and zinc ores of the Broken Hill district, on the Cape to Cairo Railway, about 300 miles N.E. of the Victoria Falls [27], [28]. The country here is a peneplain worn down in a sedimentary series consisting mainly of limestones with a few beds of sandstone. Ridges of sandstone and also a few residual *kopjes* (small hills) of altered limestone, carrying ore minerals mainly of lead and zinc, rise above the peneplain. These kopjes are, as a rule, about 300 ft. in diameter and rise from 75 to 90 ft. above the general level of the peneplain. They are composed of badly-

weathered limestone, with clay and other residual materials, and have been proved to contain oxidized ore of lead or zinc, or both together, to a depth of 150 ft. This ore has been shown by boring to pass down into sulphides to a depth of at least 300 ft. [29]. The metalliferous minerals of the oxidized ores consist for the most part of hemimorphite and cerussite with some hydrozincite, limonite, wad and other minor minerals. Among the less common minerals are descloizite, vanadinite, pyromorphite, and a number of rare zinc phosphates, such as tarbutite ($Zn_3.P_2O_8.Zn(OH)_2$), hopeite and parahopeite ($Zn_3.P_2O_8.4H_2O$) [30]. The descloizite is apparently associated with the main oxidized ore-bodies, and occurs in fairly large quantities in pockets up to an inch in width, and as massive seams and incrustations, mixed with limonite, and before its value was appreciated, many tons were thrown on the dump. The vanadinite has rather a curious mode of occurrence. Traversing the limestone kopjes in places are caves, the floors of which are covered with travertine and bone breccias; metalliferous solutions have percolated through these breccias and reacted with the phosphorus of the bones to produce pyromorphite and the rare phosphates mentioned above. With the pyromorphite is associated vanadinite, which occurs in considerable quantities as botryoidal masses, almost always as hopeite, and accompanied also by limonite and, to a less extent, by descloizite, hydrozincite, wad and other manganese oxides. It is suggested that quite a large amount of vanadium minerals could be obtained here, either by hand-picking or by treatment of the lead-zinc ores.

The reserves of oxidized lead and zinc ore on the property in June, 1922, were reported to be 650,000 tons, containing about 25% zinc, from 2 to 10% lead and from $\frac{1}{3}$ to 1% vanadic oxide. The reserves of sulphide ore were 104,000 tons. In addition, it was estimated that there were in No. 1 kopje about 60,000 tons of high-grade lead ore, containing about $\frac{3}{4}$% vanadic oxide. Of vanadium ore proper there were 1,396 tons at the smelters, with an average

content of 8·7% of vanadic oxide, and 6,221 tons of dump ore averaging 5·3%. A contract for selling this ore is in operation [31].

Tanganyika Territory

Mottramite ores are known, and some have been mined, in Tanganyika Territory.

Union of South Africa

South-West Africa

A number of deposits of vanadium ore occur in the northern part of South-West Africa, and all lie roughly near a line running N.W. to S.E. between Uris and Berg Aukas, a distance of about 60 miles. No deposits have so far been proved to any depth. They are in or near dolomite formation, generally in the form of *sandsacks* in which frequently chert débris is mixed, and sometimes the sandsacks are found in the contact between the chert and dolomite. So far all deposits have been found to be surface occurrences only, and their origin is still doubtful.

The places where payable vanadium ore has been found are Uris and Karavatu (in the N.W. belonging to the Otavi Exploring Syndicate); Tsumeb West (belonging to the Otavi Mines and Railway Co.); Nosib, Uitsab, Oliphantfontein, Abenab and Berg Aukas (all in the South-West Africa Co.'s territory). Nosib, which was originally opened up as a copper mine, has been temporarily abandoned as unpayable. Karavatu, Uris, Oliphantfontein and Berg Aukas are, or will be shortly, exhausted. Uitsab is being opened up. The other deposits are still being worked.

There is a distinct differentiation between the N.W. and the S.E. deposits: the former are of mottramite or vanadate of copper-lead with very little or no zinc; the latter contain vanadate of lead-zinc, with hardly any copper. Where zinc does occur in the mottramite deposits it is only in their lower parts.

The ores are jigged, and the products are shipped as

concentrates. That from Uris and Karavatu contains 17 to 19% vanadic oxide; 8 to 10% copper; and 38 to 44% lead. That from the other mines, except Tsumeb West: 19 to 21% vanadic oxide; 12 to 14% zinc; and 47 to 50% lead. The concentrate from Tsumeb West was stated by the Otavi Mines and Railway Co. in 1913 to contain 10% vanadic oxide.

The total yield from all of the above deposits (except Tsumeb West) to the end of February, 1923, was 3,200 tons, of which roughly one-half was vanadate of copper-lead, and the other half vanadate of lead-zinc. Further information will be found in reference [32].

Transvaal

At the Doornhoek lead mine, Marico district, Transvaal, vanadinite occurs associated with cerussite, pyromorphite, minium and massicot. It lines vugs and cavities in the principal ore-body. The largest of these was a flat inclined cavity, 15 ft. long, which probably yielded about one ton of vanadinite.

At Kaffirskraal No. 214, about 14 miles east of Ottoshoop, in the same district, vanadinite is the principal and sometimes the only ore present, although as a rule it is intimately associated with galena and other lead ores. The deposit, which is in the uppermost portion of the dolomite series of the Transvaal system, is of a bedded type, and consists of soft, blackish-brown manganese earth or wad formed by replacement of dolomite; it contains talc and wollastonite, which were originally present in that rock. The manganese earth is regularly interstratified with shale, banded shale, shaly chert and chert. There are numerous minor folds, so that the beds follow a wavy course. Two dykes of a highly altered igneous rock of intermediate composition intersect the dolomite series. The principal vanadinite workings lie between these, and the deposits are almost certainly connected genetically with them. The vanadinite, in well-formed hexagonal crystals, and in aggregates of

such crystals, occurs in irregular layers conforming to the bedding of the manganese earth and associated rocks, in steeply inclined veins cutting across the bedding, in irregular pockets and vugs—the latter sometimes lined with quartz crystals—and as an incrustation on joint planes in shale and chert.

The vanadinite is obviously of secondary origin, having doubtless resulted from the alteration of galena. Its formation and present distribution are to be attributed to the activity of descending oxygenated waters, the mineral being found wherever conditions were favourable to the circulation and damming up of such waters.

Vanadinite is rarely found in direct association with galena, but from the Christmas section workings magnificent specimens have been obtained, in which residual cores of galena are enclosed by concentric crusts of cerussite, pyromorphite and vanadinite, arranged in the order named.

The deposit has been proved by surface and underground workings. In Block A of the incline section workings, vanadinite, unaccompanied by other lead minerals, occurs in well-defined layers in manganese earth, or in ferruginous cherty shale or chert interbedded with it, there being in places as many as six distinct layers, ranging in thickness from ½ to 6 in.

In Block B the vanadinite is intimately associated with pyromorphite, galena and cerussite. In Block C vanadinite occurs as an incrustation on joints and fractures in cherty shale, or in isolated pockets and thin seams, averaging 6 in. in thickness, pyromorphite being almost entirely absent. In the Christmas section the vanadinite occurs partly in layers in manganese earth, and partly as an incrustation on joints in shale and shaly chert.

In 1921 the reserves were estimated at 4,554 tons, averaging 2·8% vanadic oxide. Eight samples, taken over widths varying from 6 to 60 ft., contained the following range of percentages: Lead, 2 to 23·2; vanadic oxide, trace to 3·8; phosphoric oxide, *nil* to 0·85. A picked sample

gave: Lead, 48·5; vanadic oxide, 5·9; phosphoric oxide, 1·6 [33], [34].

A deposit of descloizite containing over 22% vanadic oxide has been discovered near Messina [35].

AUSTRALIA

New South Wales

Small quantities of vanadium are found in various coal ashes, clays, bauxites, ironstones, etc. in the State of New South Wales, particularly in the neighbourhood of Sydney, where bricks often show the yellow efflorescence due to vanadium. None of these occurrences, however, is of any importance economically.

Vanadium occurs in lava of Permo-Carboniferous age, and numerous analyses of the lava flows of the southern coal-field, showing from *nil* to 0·07% vanadic oxide, are given in *Memoir* 7 (1915) of the *Geological Survey of New South Wales.*

South Australia

Carnotite has been found in two places in South Australia, at Radium Hill and at Mt. Painter.

Radium Hill is in the North-East district, 20 miles E.S.E. of Olary railway station. The mineralized area comprises some 4½ sq. miles. The radio-active minerals are found in lode formations traversing metamorphic gneissic, micaceous granite and granite-schist, into which dykes of granite and diorite have been intruded. The primary mineral probably pitchblende, although proofs of this are still wanting. Of the secondary minerals, carnotite is the most widely distributed, but autunite and torbernite have also been recognized. The carnotite occurs as yellow and greenish-yellow incrustations and powder on the faces, joints and cavities of a lode formation, which consists of titaniferous iron ore, magnetite, etc., and quartz in association with black mica (biotite). The dark colour of the schist

or gneiss, due to biotite, is a useful indication of uranium-vanadium minerals. The greater part of the titaniferous iron ore is composed of ilmenite. When hæmatite and magnetite are prevalent, titaniferous iron-ore and uranium-vanadium minerals are usually absent. Pyrite is present in small proportions; in the upper part of the ore-bodies it has been more or less completely converted into limonite. Traces of malachite, and an undetermined green mineral containing a small percentage of vanadium, have been detected in the limonite or oxidized upper part of the ore-bodies. Two of these lode outcrops strike N. 39° E., and are from 15 to 45 ft. apart. The thickness of one lode is given as from 2 to 3½ ft. Several parallel lodes occur, and the average width of one of these is between 4 and 4½ ft. The lodes have been mainly formed by selective mineralization of certain bands of rock, which conform to the foliation of the rocks in their immediate vicinity. In a few places the ore-bodies appear to have resulted from the filling of fissures with lode matter introduced in solution.

Crook and Blake, who made a partial examination of a specimen of the lode material, noted the presence of rutile carrying about 3% iron oxide and about 1·5% vanadic oxide. In what appeared to be an intimate mixture of rutile, ilmenite and magnetite, they also found by microscopic and chemical examination a mineral that appeared to be tscheffkimite, possibly a silicotitanate of the rare earths, which, according to Dana, is apparently always an alteration product. The predominant constituent of the ore-bodies is ilmenite, the other minerals being impregnations or incrustations. The carnotite is very similar to the Colorado mineral. When visible it is an indicator of high-grade uranium-bearing ore. An analysis gave the following percentages: Uranium oxide, 60·8; vanadic oxide, 21·4; phosphoric oxide, trace; lime, 1·3; magnesia, trace; potash, 6·6; soda, 2·3; lead oxide, 1·7; water, 5 (= 99·1). The vanadium content of the ore as mined is 0·6% only.

The discovery was made in May 1906. The property

was held by a small syndicate for a time. In 1909 a Sydney company took up the ground and started developing the deposit. By September 1911 the carnotite-bearing lode had been proved over a length of 1,825 ft. and to a depth of 50 ft. A magnetic separator plant was erected later, and in 1915, 40 tons of concentrate were produced from 212 tons of ore. Work was suspended on the mine before the end of the same year [36], [37].

Mt. Painter is in the Flinders Range, 65 miles S. of E. from Farina. Metamorphism of sediments, probably of Cambrian age, has resulted from numerous intrusions of granitic and pegmatitic dykes. The geological features of the district resemble those of Radium Hill, Olary. There are several lode formations, some crossing and others running parallel with the strike of the altered sedimentary rocks, which is approximately E.–W. The primary radio-active minerals are fergusonite and monazite. The secondary ores are more numerous. Of these the most widely distributed are torbernite and autunite; other secondary ores are uranophane, gummite, uranochre (uraconite) and carnotite. The gangue consists of quartz, hæmatite, a rhombohedral carbonate of the calcite group, fluorspar, barytes, psilomelane, and fragments of country cemented into the lode-matter, which has been introduced from below.

In the No. 6 mine of the Radium Extraction Co. of South Australia, Ltd., there is a strong ferruginous lode, striking N.–S. The hard, dense manganiferous iron ore at the outcrop proved to be a superficial skin to a mass of dense hæmatite, and numerous small veins of black manganiferous ironstone, soft friable kaolin, and subangular blocks of gneiss and pegmatite, which have suffered silicification, and a few segregations of quartz, which suggest that the deposit was apparently formed by the almost complete replacement of a zone of variable width by the agency of solutions containing iron and silica. Torbernite is sparingly distributed through the formation, and is most noticeable where streaks and patches of psilomelane and

pyrolusite occur. In one place a fault zone traverses the lode, and the best and only marketable ore yet discovered in this field occurred in this zone in the form of narrow veins of autunite and torbernite associated with manganiferous ironstone. A shoot of good ore proved to be from 15 to 20 ft. in length, and to extend downwards to a depth of 40 ft. from surface. In this shoot the ore was soft and friable, and the autunite occurred for the most part in horizontal seams and patches. The value of the ore of the principal shoot decreased below the 50-foot level to such an extent that the shoot could hardly be said to exist below that level [36], [38], [39].

In 1910 W. B. Greenwood found carnotite in some lode-matter in the district, which led to the recognition of torbernite, and ultimately to the more detailed prospecting of the field [38].

Several companies were at one time working here. Some radium was extracted, but none of the deposits were worked for vanadium, which appears to be a rather rare alteration product of the lode formations. Work was suspended at Mt. Painter in August 1914.

Vanadium ore, as yellowish-green stains and coatings in the joints and crevices of copper-bearing slate rock, and in small vugs and crevices in copper ore, has been found to a depth of 18 ft. at Paull's Consolidated Copper and other mines in the Leigh's Creek district. A sample from Paull's North mine yielded, on analysis, 0·12% vanadium, which existed in the surface as vanadium ochre [40/p. 363].

Vanadium ochre has also been found at Clarke's Mount Lyndhurst mine, Booleroo Springs, and the Mountain of Light.

At the Edelweiss or Edeberg mine, situated in the hundred of Apoinga, 14 miles south of the Burra Burra copper mine, a vertical vein of quartz, which is 12 in. thick in places, strikes N. 15° E. and carries, to a depth of 50 ft. vertical, isolated nodules and small bunches of tetrahedrite with a little azurite and malachite and sulvanite, a sulpho-vanadate of copper, an analysis of which yielded

the following percentages: Copper, 48; vanadium, 12·5; sulphur, 30; with quartz and iron oxides. A good deal of prospecting disclosed the fact that vanadium in small specks and splashes was visible throughout the formation, but not in sufficient quantities to be of commercial value, except towards the north end of the workings, whence, it is said, a small parcel of ore was raised and shipped to England. In one shaft vanadium occurred somewhat freely in a vein from 12 to 15 in. wide, striking N.E. and S.W., to a depth of from 15 to 20 ft., and at a depth of 115 ft. there was a strong siliceous formation, 20 ft. wide, containing vanadium in places. Vanadium was also found in small spots in the same formation in another shaft at a depth of 150 ft. Two samples taken from a small parcel of selected ore gave the following analyses: No. 1, copper, 10%; vanadium, 1·46%; No. 2, copper, 22%; vanadium, 3% [40/p. 50].

Western Australia

According to E. S. Simpson [41], [42], vanadium is of widespread occurrence in the ancient greenstones, laterites, coal ashes and clays of Western Australia. Analyses of the ashes from the Collie coal show from a trace to 0·21% vanadic oxide. Traces of vanadium in clays are disclosed by the yellow or green efflorescence on the surface of a brick, which has for the first time been wetted and then slowly dried.

Roscoelite (vanadium mica) and an undescribed chrome-vanadium mica are moderately plentiful in the gold ores at Kalgoorlie. Analyses have given from 0·32 to 1·21% vanadium trioxide. Pucherite (vanadate of bismuth) has been found in concentrate from a gold mine at Niagara. Vanadinite has been detected in auriferous quartz from Burbanks, Coolgardie; Menzies; Pinyalling, and elsewhere, and it occurs in considerable masses associated with pyromorphite at Gregory Range.

CHAPTER III

SOURCES OF SUPPLY OF VANADIUM ORES (*continued*)

(*b*) FOREIGN COUNTRIES

EUROPE

CZECHOSLOVAKIA

SOME vanadium has been produced from the silver and other ores carrying pitchblende or massive uraninite at Joachimsthal, Bohemia, but never in important amount. The production was made in the infancy of the industry many years ago, and no figures appear to have been recorded.

At Joachimsthal, both N.–S. and E.–W. lodes occur in country rocks, consisting for the most part of mica-schists, enclosed between masses of granite. Pitchblende occurs in both systems of lodes, but more especially in the N.–S. system, or near the intersections of the two systems, and the mineral is associated with silver-cobalt-nickel-bismuth ores. The N.–S. (newer) veins become enriched where they pass through the porphyry or included limestone, which is not the case with the older E.–W. veins [25/p. 436].

The vanadium may be regarded as an alteration-product.

FRANCE AND LUXEMBURG

As already stated, vanadium compounds are found in certain residual formations, such as bauxites, and in shales, clays and other sediments, including the minette iron ores of Eastern France and Duchy of Luxemburg. They are never present in any great quantity, and it is probably only

due to the large-scale commercial working of these rocks that their presence has attracted so much attention.

The presence of vanadium in bauxite [6/p. 727] was first noticed by Sainte-Claire Deville in 1859, and was reported by him in the *Comptes Rendus*, but no commercial production has ever been made from these rocks. Since then the element has been shown to have a wide distribution in the minette iron ores, and at Le Creusôt [6/p. 721], [43] it has been extracted on a commercial scale, particularly from slags derived from the smelting of the oolitic ores of Mazenay (Saône-et-Loire). The state of combination of the vanadium in the ores is not known, but the minettes may contain any amount from 0·1 to 2% vanadic oxide. On smelting, some of the vanadium goes into the slag, but the iron takes up a similar proportion, nearly all of which, however, passes along with the phosphorus into the slag in the basic converter. The following figures were obtained by von Blum [44] for some Luxemburg ores: Minette containing over 0·1% vanadium gave a pig-iron with an average of 0·18%, and a slag with an average of 0·12% of the metal. The converter slags from this iron contained an average of 0·158% vanadium, while the steel contained as little as 0·01%.

The amount of vanadium in the slags varies considerably; in one slag from Luxemburg as much as 2·56% vanadic oxide was formed, and the average figure for Le Creusôt slags has been taken at about 1·5%. However, the total weight handled was large, and it was estimated that about 59 tons of vanadium were contained in the slag made in one year at Le Creusôt. This was the largest source of the metal then known, and production was carried on until 1885, when demand for vanadium for aniline black fell off.

Germany

Vanadium has been detected in the *Kupferschiefer* of Mansfeld, Central Germany. Its presence is probably due to infiltration; and the immediate cause of its preci-

pitation is believed to be the reducing action of the organic matter of the fish whose remains are found in this bed [45]. Lindgren says the kupferschiefer was laid down in a shallow sea full of decaying vegetable and animal remains into which cupriferous waters from the surrounding littoral were discharged, most likely sulphate solutions derived from the eruptive of the early Permian epoch. Although there are very strong arguments for a syngenetic origin, the characteristic presence of nickel, cobalt, vanadium and selenium recalls the epigenetic deposits in sandstone so abundant around the shores of the Permian sea, in Bohemia and Russia [46/p. 581].

Russia

Vanadium ores have been reported from some places in the Ural Mts. [6/p. 726], and from the Alai Mts. in the north of Russian Turkestan [47]. The former occurrences consist of volborthite associated with copper phosphates at the outcrop of several veins, but nothing further seems to be known about them. The largest deposit of the Alai Mts. region is at Tjua-Mujun in the Andijan district of the Ferghana Government (old style), and about 50 miles from Fedtschenko, the nearest railway station. The ore-body is a large but very irregular pipe in Palæozoic limestone with a gangue of calcite and strontium-bearing barytes. The ores are tyuamyunite (uranyl-calcium vanadate), turanite (copper vanadate), malachite, hæmatite, and five or six new minerals containing uranium, vanadium, bismuth, arsenic and lead; a mineral from this locality named ferghanite is possibly identical with tyuamyunite.

The deposit is said to have been worked by the Chinese for copper. About the year 1911 vanadium ore was shipped to Petrograd, where it was converted to ferro-vanadium. Work soon ceased, however, owing to the death of the proprietor, and the mines do not appear to have been re-opened. No figures of output are available.

Spain

Ores from Spain played an important part in the early history of vanadium steel, and it was from these ores that Kent Smith produced the first button of ferro-vanadium [48]. However, the output has never been large, and of late years has entirely ceased, owing to the discovery of cheaper and more easily worked ores from other countries. But though such a large proportion of the world's supply at one time came from Spain, there is a surprising lack of

Analyses of Spanish Vanadium Ores

Vanadinite.	Per cent.	*Chileite.*	Per cent.	*Descloizite.*	Per cent.
Vanadic oxide	11·49	Vanadic oxide	13·50	Vanadic oxide	22·46
Lead oxide	34·15	Lead oxide	54·90	Lead oxide	54·70
Lead sulphide	1·43	Lead chloride	0·30	Zinc oxide	2·04
Ferrous oxide	13·17	Copper oxide	14·60	Copper oxide	0·90
Manganese oxide	0·77	Arsenious oxide	4·60	Manganous oxide	5·32
Zinc oxide	0·62	Phosphoric oxide	0·60	Manganese dioxide	6·00
Molybdenum oxide	trace.	Sand or clay	2·00	Sand and clay	3·44
Calcium carbonate	0·74	Iron peroxide, alumina, etc.	3·50	Iron peroxide, alumina, etc.	1·50
Siliceous matter	35·67	Lime	0·50	Loss on ignition	2·20
Silver	3·5 oz. per ton	Loss on ignition	2·70		

information concerning the ore deposits, and a considerable amount of confusion seems to exist among writers on vanadium as to whether the deposits are in the south or north of Spain, or both.

It seems clear, however, that the only mines of any importance were at Santa Marta [48], [6/p. 726] in the Estremadura Division, at a distance of 25 miles from the railway station of Safra, and 65 miles from the town of Badajos. The ores belong to the vanadate class, and originate as usual in the oxidized part of lead veins. The principal deposit is a thin vein with a maximum width of 4 in. cutting through clays which are also rich in vanadium. The content of the ores was between 4 and 5% vanadic oxide, and by hand-dressing the tenor was raised to about 12% vanadic

oxide [49]. A portion of the ore, a mottled reddish sandstone, contains 6% vanadium, the state of combination of which is not given [48].

Other minerals occur besides vanadinite, and the analyses of some of these are given above. The vanadinite ore was preferred to that of Zacatecas, Mexico, on account of its comparative freedom from arsenic. Analyses of Spanish vanadate ores are given in table on p. 31 [49].

SWEDEN

In addition to the vanadium occurring in the titaniferous ores of Taberg, Sweden, already referred to, and from which a little vanadium has been recovered, according to a report issued in the *Stockholms Dagblad* in 1917 [50], vanadium had been discovered in the ash of coal in Billingen Skaraborg Län. The coal was said to be of good quality, but to occur in beds only 4 to 8 in. thick. The ash content was 1%, and of this 40 to 50% was vanadic oxide. An output of 10,000 tons of ash or 20 tons of vanadium per annum was expected. The thin beds are probably asphaltite and not coal, but no further information has been published on the subject.

AFRICA

ALGERIA AND TUNIS

Vanadate minerals, apparently occurring in the upper oxidized parts of lead lodes, are reported from Oran in Algeria; from a mine in Tunis; and from other places in North Africa.

CONGO FREE STATE

A deposit at Ruwe, in the Congo Free State, described by Ball, contains in a sandstone a most curious association of ores yielding gold, platinum, silver, palladium, vanadium, nickel, lead and copper, the last two metals as vanadates [46/p. 576].

NORTH AMERICA

Vanadium ores occur in the continent of North America, in the United States and Mexico, and are chiefly confined to two areas; (1) the states of Colorado and Utah, where the ores are roscoelite and carnotite; and (2) the southern region of the Rocky Mt. Chain in the states of Arizona and New Mexico, and in the northern and central portions of Mexico, where the ores all belong to the vanadate class, and are associated with deposits of lead ores.

There are, in addition, a few more occurrences of little importance which are detailed below.

Mexico

The vanadium ores of Mexico are found along the main Cordilleran region from the state of Chihuahua in the north, to Hidalgo in the south. They are always associated with lead and copper deposits, and contain sometimes vanadinite, sometimes cupro-descloizite (ramirite) as the principal mineral. All ore mined before 1910 was shipped to Europe, but the production had always been small, and is exemplified by the recorded export of 860 lb. of cupro-descloizite ore containing 10·5% vanadium from Charcas [51], in the first eight months of 1903, and 11 tons from the same place in 1905.

The ores appear to be in fair quantity and to be capable of concentration with reasonable ease, but their high arsenic content has always been against them [51], [52], [53].

Vanadinite ores are reported from the following places:

State of Chihuahua: Villa Rosales (San Francisquito mine), Cuchilla (Aurora and San Pedro mines), Parado, Coyame and Iturbide; State of Guanajuato: Pozos and San Luis de la Paz; State of Guerrero: Tasco; State of Hidalgo: Pachuca (San Antonio and El Puerco mines) and Zimapan; State of San Luis Potosí: Catorce (La Concepción mine), Charcas and Matehuala; State of Zacatecas: Ojocaliente and Zacatecas (district) [53].

The cupro-descloizites (or ramirites) of Mexico are closely allied to chileites, and the following is given by Curran [53] as a representative analysis: Vanadic oxide, 13%; lead monoxide, 55%; copper oxide, 14·6%; arsenic trioxide, 4·6%; sand and clay, 2%.

Vanadium ores associated with wulfenite have been found near Zacatecas [48/p. 671], and in this region occurs a deposit of mimetite, a complex lead mineral, containing 2·5% vanadium [54], [55].

The purest Mexican ores appear to be the vanadinites of Chihuahua [53], and it is said that these can be easily concentrated to a content of 18% vanadic oxide. The Zacatecas ores are reported to carry 4% vanadic oxide as mined, and 64% lead; they exist in large bodies, but often contain a considerable quantity of arsenic.

United States

The principal deposits of vanadium in the United States are in the states of Colorado and Utah. The roscoelite deposits are described first, as vanadium is derived directly from them; a description of the carnotite deposits follows, vanadium being only a by-product of the ores, which are mined for the production of radium. The vanadinite deposits are described last, as economically they are not so important as the roscoelite and carnotite deposits.

Deposits of Roscoelite at Placerville and Vanadium, Colorado.—The roscoelite deposits of Placerville, San Miguel Co., Colorado, are found extending for about 10 miles alongside the San Miguel River and auxiliary creeks, from Brown on Leopard Creek, 4 miles N.E. of Placerville, to a point on Bear Creek, 3 or 4 miles due south of Vanadium (formerly called Newmire).

While vanadium ores are more or less restricted to the above area, deposits similar to those of Placerville have been reported from White Cliffs, near Telluride, 10 miles east of Vanadium; and, in 1920, they were being worked by the Colorado Vanadium Co. [56/p. 812].

The region is an eastward continuation of the Uncompahgre Plateau, and consists of horizontal sedimentary rocks belonging to the Dolores (Triassic), McElmo and La Plata (Jurassic) formations. The deposits are found cropping out along the sides of the deep valleys or canyons of the region. The portion of La Plata formation, which contains the vanadium deposits, is between 35 and 60 ft. thick, and consists of two beds of sandstone, separated by thin limestone. The vanadium deposit occurs in the lower sandstone beds, and is probably made up of two seams, with unconformity between them. The sandstone is in places cross-bedded, and although usually fine-grained, it sometimes contains pebbles as large as small peas. Ordinarily it is cemented with calcite, and is very friable. Near the ore deposits the beds are cut by a few basic dykes, such as dolerite and basalt, and there is some faulting. These dykes may be connected with laccoliths of diorite-porphyry lying to the east of Sawpit and north of Vanadium. The vanadium-bearing rock is a fine even-grained sandstone, from dull green to almost black in colour, usually becoming darker as the proportion of vanadium increases, except where carbonaceous matter, iron oxide, etc. may be present. A yellowish colour usually indicates carnotite. Where the sandstone is cross-bedded, there are different shades of green and black, and some of the ore shows many small sage-green dots, which appear to be nuclei, around which the roscoelite has formed. In many places bands of nearly colourless quartzite (" bone "), from ½ to 4 in. thick, alternate with the green sandstone. A section at the Rio No. 1 claim was as follows: Sandstone, ironstained, partly quartzite, 3 in.; dark vanadium-bearing sandstone, 4 in.; " bone " or quartzite, 2½ in.; dark vanadium-bearing sandstone, 4½ in.; " bone," 2½ in.; dark vanadium-bearing sandstone, 3½ in. The silicification seems to be, at least in part, later than deposition of the roscoelite, for the quartzite encloses vanadiferous sections of the sandstone.

Examined microscopically, the vanadium-bearing sandstone is seen to be composed of a number of grains of quartz

cemented by roscoelite and some calcite. The former has probably generally replaced the latter. In addition to quartz, there are a few grains of felspar, but some of the felspar grains have been replaced by calcite, roscoelite, or roscoelite and quartz. In addition there are a few grains of chalcedony, vein quartz, an exceedingly fine-grained quartzite, zircon and tourmaline [57/pp. 11–14], [58/p. 149], [59/p. 51].

Carnotite is very sporadic in occurrence in these deposits; it seems to have been leached from the surrounding rocks, and is usually found in cracks and joints, associated with blue and black vanadium compounds, among which appears the sulphate, kentsmithite, a body of which was discovered some years ago in the Beattie No. 3, at Fall Creek, samples averaging 25% vanadic oxide [48/p. 669].

The vanadium deposits both vertically and laterally grade out into deposits having a lighter green colour, due to chromium-mica, probably mariposite. Besides chromium the vanadium ore is also sometimes associated with copper, in the form of chalcocite and malachite. The deposits vary in thickness from a few inches up to 30 ft. and are flat, lens-shaped or tabular, generally from 600 to 700 ft. wide, with local thickenings and thinnings. At Bear Creek a drift was cut for 1,200 ft. in vanadiferous sandstone.

The deposits bear a very direct relationship with a plane, apparently one of unconformity, in the lower bed. Along this plane is a very rich black shaly seam or vein up to ¾ in. thick, composed of roscoelite and quartz, with a little pyrite, and, in places, a black substance which may be organic. On both sides of this vein the sandstone is impregnated with roscoelite, with a little pyrite, generally oxidized, and what may prove to be a little organic matter [58/p. 152]. It is probable that the dykes already mentioned had much to do with the mineralization, although the richest known deposit on Bear Creek has no visible connection with any dyke. The plane of unconformity seems to have acted as a channel for the passage of the thermal

solutions which brought in the quartz and the vanadium and chromium compounds.

There are many thousands of tons of sandstone which will show between 1 and 2%, and much more between 0·5 and 1% vanadium [58/p. 156]. Transport is easy, as the district is traversed by the Rio Grande Southern Railroad. The Primos Chemical Co., which formerly owned the principal deposits on Bear Creek, had a plant at Vanadium with a capacity of 30 tons of sandstone per 8-hours' shift, for converting the ore to ferric vanadate, which was shipped east for conversion to ferro-vanadium. The property is now owned by the Vanadium Corporation of America, but is not being worked at present.

Carnotite ores of Colorado and Utah.—Deposits of uranium and vanadium ores occur in the S.W. part of Colorado and the S.E. corner of Utah. They are widely distributed on both sides of the Grand River, and cover a very large area, extending from the San Rafael Swell (or dome) in the N.W. to Placerville and Dolores, Colorado, in the S.E., and from Cisco, Utah, in the N.E. to the Henry Mts., and probably beyond, in the S.W. The ores are mined principally for the production of radium, whilst uranium and vanadium are obtained as by-products.

The rocks of the region are sedimentary. The oldest are the " Red Beds " of the Dolores formation, which are of Triassic age. Above these is La Plata formation, succeeded by the McElmo formation, both of Jurassic age, which contain the uranium-vanadium deposits. The Dakota Sandstone, of Cretaceous age, rests on the McElmo formation and above it are the Mancos Shales, also of Cretaceous age. On the S.E. the Jurassic rocks are flat or gently folded, and form a region of mesas or plateaux. On the west side of the region the dips are steeper, forming an area of " hogbacks " (escarpments with steep dip and slope).

The roscoelite ores of Placerville occur, as already mentioned (*see* p. 35), in La Plata sandstone, while the carnotite ores are more particularly associated with the McElmo rocks, although a few deposits have been found

in the older Red Beds. The deposits are usually lenticular in form, the lenticles often being disposed obliquely to the bedding. They usually extend more than 100 ft. in length and width, and the thickness ranges from a few inches to 14 ft.—the average being 4 or 5 ft.

Each lenticle or pocket yields from a few hundred pounds to as much, in one instance, as 2,080 tons. As a rule, the high-grade ore is only a few inches thick. Frequently small funnel-shaped pockets (the "bug-holes" of the miners) of high-grade ore enter the upper portions of the ore-bodies, inclined at a low angle, although a few enter the lowest part of the deposit, and end abruptly in ore. They are from 2·5 in. in diameter, and sometimes 30 to 40 ft. long. The walls are usually incrusted with quartz or gypsum. The filling is usually a soft yellow clay, containing a high percentage of carnotite, or it may be a blue or black vanadium ore. At their upper end the vugs open out into a funnel-shaped mass of soft sandstone, heavily impregnated with ore which gradually merges into country rock [59/p. 30]. Besides carnotite, which is probably an alteration product of pitchblende [60], other vanadium minerals occur, such as hewettite, metahewettite, volborthite, calciovolborthite, pintadoite, uvanite, kentsmithite and roscoelite. The ores are always found in sandstones which often contain fossil wood, partly silicified and partly carbonized, the latter portion being often replaced by material rich in uranium and vanadium minerals. In Bull Canyon, south of Paradox Valley, a tree trunk between 50 and 100 ft. long was replaced by a mass of rich carnotite ore [61/p. 680]. The greater part of the ore, however, replaces the calcite or gypsum cement of the sandstone, and lines cavities and joint- and bedding-planes in the rock, which are often false-bedded.

More than one theory has been put forward to account for the origin of the ores, the most generally accepted one being that of Hillebrand and Ransome [57/p. 17], *viz.* that the ores were originally disseminated through the sedimentary series in which they are found, or, possibly,

through the Cretaceous sandstones and shales overlying them, and that they were concentrated at certain horizons —determined by the distribution of fossil wood or by impervious shale beds—by the action of percolating ground water during the present cycle of denudation. Lindgren supports this view, for he says [46/p. 579]: The vanadium deposits of Colorado and Utah "are probably products of concentration, by surface waters, of small quantities of the metal distributed through littoral beds or land deposits of sandstone and clays." In some experiments on the formation of these ores, Notestein has shown [62] that carnotite is readily soluble in ground waters carrying free sulphuric acid and alkali sulphates and bisulphates, and that calcite readily precipitates vanadium and uranium from vanadyl and uranyl sulphate solutions. This helps to explain the association of carnotite ores with gypsum.

Other views are by Fleck and Haldane [63] and by Hess [61/p. 685].

The Eastern or Plateau Area, mainly in Colorado.—The carnotite deposits in San Miguel and Montrose counties, Colorado, have been known for many years. In 1881 they were tested for gold, silver and copper. In 1896 it was discovered that the mineral contained uranium. In 1899 two Frenchmen visited Paradox Valley, collected specimens and sent them to C. Friedel and E. Cumenge in France, who examined them and announced the existence of a new mineral, which they named carnotite [59/p. 18].

The area includes the Dolores and Disappointment districts, Paradox Valley, Long Park, and La Sal Mts., Utah, and, extending northward, past Uranium, to the town of Gateway. It is the most developed and the best known area, reaching 40 miles from north to south, and 20 miles from east to west. The average shipping ore contains 2½% uranium oxide (U_3O_8) and 3 to 4% vanadic oxide. The most typical ore is a sandstone with a noticeable yellow colour (carnotite), and with many small kidneys of brown sandy clay. There are besides dark blue, brown and black vanadium ores, mostly undetermined minerals,

the soft high-grade carnotite ore of the "bug-holes," the same kind of ore crystallized with gypsum, and red calcium vanadate, some in radiated form, and some mixed with carnotite and blue vanadium ore.

In 1916 the mining claims of the National Radium Institute were at Long Park, a plateau lying north of East Paradox Valley, about 3 miles long and ½ mile wide. On the Maggie C—the most important claim—the main body of the ore consisted of an irregular, but rather elliptical, pocket, measuring some 350 ft. in length by 200 ft. at the widest part, with its main axis trending N.E. There were three rich spots within this pocket. Two smaller pockets were found along the rim rock, south of the main lens, and one near the entrance to a main adit. The production from these various pockets was as follows: Main open cut, 265 tons; large stope, 150 tons; tunnel, 210 tons; small pockets on rim, 8 tons; small pockets on gulley, 10 tons; other underground workings, 7 tons; total 650 tons.

On the Florence claim, in one place, the ore occurred in thin bands or laminations in a clearly bedded sandstone. The bands of carnotite were $\frac{1}{32}$ in. to 4 or 5 in. across, the extremely thin bands being nearly pure carnotite, and the thicker ones being sandstone, so impregnated with carnotite as to carry from 2½ to 3½% uranium oxide. The sandstone below the bands of carnotite was in many places highly impregnated with vanadium, the whole forming a mineralized band or vein 2 in. to 2 ft. thick. This claim ranked next to the Maggie C in productiveness, yielding about 140 tons. In one portion of the Great Western claim, which ranked third in yield, the ore was found in a loose breccia, different-sized pieces of carnotite-bearing sandstone being indiscriminately mixed with sand, clay and angular fragments of barren rock. On the Medea claim, in one place, the ore was rather coarse grained, closely resembling that on the Maggie C, and contained thin stringers of calcium vanadate and vanadic oxide, rarely more than ½ in. thick, which generally crossed the bedding of the sandstone and seemed to be small fissure veins [64/pp. 9–17, 44].

In several localities the ore is found in cylindrical sleeve-like pockets or " bug-holes," 2 to 4 in. in diameter, filled with canary-yellow high-grade carnotite. The ore when first removed is soft, so that it can be moulded in the hand, but on exposure to the air it becomes hard and brittle. At these pockets the ore is surrounded by a hard envelope of ferruginous sandstone about 2 in. thick, outside which the sandstone is soft for some distance. Sometimes the ore is surrounded by soft sandstone, and sometimes the envelope is largely composed of gypsum. In several cases the ore-bearing sandstone contains carbonaceous material that has a yellow coating. This carbonaceous material is radio-active, but contains no vanadium [59/p. 24].

At Club camp, close to Gateway, on the west rim of the San Miguel Canyon, four miles above its junction with the Dolores, 45% of the total production of the region was being mined by the Standard Chemical Co. in 1920 from ore located by diamond drills, and 10,000 ft. of drives and crosscuts had by then been driven.

The Cliff mine is in rim rock and lies 500 ft. above the floor of the Sauce Basin, at an altitude of 6,100 ft. A layer of carnotite-bearing sandstone extends 500 ft. along the face of the cliff. The pocket of ore is almost horizontal at the surface, but at 15 ft. in it begins to dip slightly to the north. At the top is white sandstone, then comes 4 to 6 in. of carnotite ore showing thin dark-grey and black layers of vanadium ore. Below this is similar vanadium ore, carrying carnotite, 3 ft. in thickness, and having in places narrow bands of decomposed quartzite [59/p. 25].

On the north side of East Paradox Valley, about half-way between Coke Ovens and Long Park, there is a body of ore, 2 to 3 ft. thick, carrying intermingled carnotite; calcium vanadate; carbonaceous material that is highly radio-active, and is also rich in vanadium; blue, black and grey ores of vanadium; and " bug-holes " containing carnotite. A shipment of 13 tons carried 3·43% uranium oxide and 13·66% vanadic oxide [59/p. 26].

On the south side of the same valley (East Paradox)

a number of claims are located on a faulted segment of the carnotite strata. Several of the claims at one time produced much vanadium. The most important claims in 1920 were the Jo Dandy and the Monogram, owned and operated by the Standard Chemical Co. The former claim, in 1912, was believed to be nearly exhausted [59/p. 27], but in 1920 it was a steady producer, a number of ore-bodies having been opened up by adits, some of which were being worked under 140 ft. of cover. The low-grade ore was being concentrated [65/p. 758]. According to Moore and Kithil [59/p. 77] a " bug-hole " at the Jo Dandy contained some blue-black and red vanadium ore, and some of the bug-holes were surrounded by layers of gypsum ⅛ to ¼ in. thick.

Prospecting in the Eastern or Plateau district is by jackhammers or by diamond drills, and mining by a room-and-pillar method, the low-grade ore being left as pillars. One estimate gives a possible reserve in this area of 100,000 tons of ore containing 1·5% uranium oxide and 4·5% vanadic oxide. The ore is treated either at Denver, or in the Eastern States, and the products are sold as ferro-uranium, ferro-vanadium, radium and vanadium salts [65].

The Area between La Sal Mountains and Green River, Utah.—At Richardson, on the Grand River, 27 miles from Cisco, vanadium ores are associated with a fracture zone in the Red Beds (Triassic), from 5 to 25 ft. wide, striking N. 60° E. and dipping S.E. 70°. The ore minerals have been proved for a length of 1,000 ft., and to a depth of 32 ft. The ores, containing vanadio-arsenates of copper, barium and calcium, together with a little amorphous carnotite, occur in radiating aggregates, filling cavities and cracks in the fracture zone, and impregnating blocks of sandstone and some sandstone beds on either side of the belt. The carnotite was probably later than the non-uranium-bearing vanadates [66].

Pintadoite occurs as an efflorescence on the surface of vanadium-bearing sandstone at Pintado Canyon, near La Sal Mts. [67/p. 14].

The Green River and San Rafael Swell District, Garfield County, Utah.—Along the S.E. side of the Swell or Dome in Garfield Co., Utah, uranium and vanadium ores occur at two horizons, the upper one in the McElmo formation, and the lower one in the Triassic shales, not far from the Shinarump conglomerate. The former occurrence is about one mile to the east of the gorge of the San Rafael River, 15 miles S.W. of the town of Green River, on the Rio Grande Railroad. The ores are found at three different levels within a thickness of 100 ft. in the McElmo formation (Jurassic); from 200 to 250 ft. above the Red Beds (Triassic), and also exposed in the tributary gullies for a distance of at least two miles along the strike. The deposits occur in a coarse, loosely consolidated, cross-bedded sandstone, which is in places finely conglomeratic. The sandstone is cemented with calcite, and carries much petrified wood, many imperfect plant remains that appear to have been reeds, and many fossil bones. Some of the petrified wood is in logs 2 to 3 ft. in diameter, and 10 ft. or more in length. The plant remains seem to occur largely along one horizon in the sandstone, and the carnotite is closely associated with them. All the deposits examined except one were seen to be associated with faults. Their presence with the organic matter seems to be fortuitous, and due to the convenient cavities provided by its decay and removal, or to its cracking [66], [68].

The ores are of four types: Yellow carnotite, found mainly in cracks; dark-brown siliceous ore impregnated with carnotite; a black ore associated with carbonaceous material and carrying stains of carnotite; and a greyish-brown laminated sandy shale rich in vanadium and with a little uranium. Parts of the deposit show mixed ores. The ore probably contains between 1 and 2% uranium oxide and about 2·5% vanadic oxide. In 1912, 346 tons of ore was shipped from Green River, Thompsons and Cisco. The returns, however, did not cover expenses [59/pp. 14–16].

Thompsons, Grand County, Utah.—Thompsons is a station on the Rio Grande Railroad, about 25 miles to the

east of Green River. The deposits are about 16 miles S.E. of the station. They are almost flat-bedded, and form a connecting link between those of the San Rafael Swell on the west and those at Richardson on the S.E. The carnotite-bearing zone of the sandstone is in one place 8 or 9 in. thick, and is overlaid with a strip of carbonaceous material. Two feet below the carnotite is a layer of what appears to be roscoelite, 2 ft. thick. Here and there in the sandstone are small pockets of red vanadium ore, probably calcium vanadate, showing imprints of fossil-fern leaves and stems. Other pockets show a mixture of carnotite and dark vanadium ore, embedded in and between thin layers of crystallized gypsum [59/pp. 16–18].

Open-cut workings between 1904 and 1913 produced little ore. No work appears to have been done on these claims lately.

Henry Mt. Area, Garfield County, Utah.—Further S.W. from Temple Rock, Utah, uranium and vanadium ores are found in the Henry Mt. in rocks believed to be the equivalent of the McElmo formation of Western Colorado. The principal minerals are carnotite, hewettite and meta-hewettite, with some chromium compound and selenium, which occurs in sandstones associated with plant remains and carbonized wood [67/p. 630]. The Standard Chemical Co. has done a considerable amount of development work on some of the claims, and was the first to ship ore from here in 1914 [69].

Rio Blanco County, Colorado.—Carnotite is found at Coal Creek, Rio Blanco Co., at the summit of a hogback ridge formed by the lowest and most massive of the sandstones, which are of Jurassic age [69]. In the principal group of deposits, the mineral is associated with fossil or silicified wood. The carnotite is in the form of a bright yellow film or crust with the appearance of having been deposited from solution, coating the silicified wood and filling cracks in it, and to a less extent in the neighbouring sandstone [70], [59/p. 10].

Routt County, Colorado.—Carnotite is found on the

summit and flanks of the highest hogback at the southern foot of Blue Mt., 2 miles west of Skull Creek, Routt Co., Colorado. The ore occurs in the upper massive beds of a coarse white sandstone (Jurassic), showing cross-bedding. It occupies a brecciated zone in the rock, the minerals being concentrated in, or evidently distributed from, the coarser joints or more porous layers, and sometimes impregnating the more massive sandstone. Vanadate of copper, malachite, azurite, copper selenite and brochantite (?) are found with the carnotite. Roscoelite is also probably present in one place [71], [59/p. 11]. Gale did not note the association of silicified wood in this locality [71].

The deposit on Uranium Hill, on the west side of Skull Creek Basin, sometimes occurs as incrustations, and in many places is cemented with gypsum [59/p. 12].

Eagle County, Colorado.—In Eagle Co., 7 miles S.E. of the town of Eagle, Colorado, silver ore occurs carrying vanadium. The ore is a dark green sandstone, rather like the darker types of roscoelite of the Placerville district, and assays from 25 to 1,000 oz. silver per ton. The vanadium ore, usually, but not invariably, low in silver, contains coarsely crystalline layers. The high-grade silver ore is more compact, usually darker, and has blue-black spots and stains, due probably to silver bromide. The ore-body, which is more than 19 ft. in thickness, dips E. 34°, and has been proved by adits for a length of 40 ft. It contains 0·21 to 2·66% vanadic oxide. A sample taken across the breast of the lower drive gave 0·94% vanadic oxide. No attempt to recover the vanadium had been made when the report on the locality was written [59/p. 53].

Garfield County, Colorado.—In Garfield Co., N.W. Colorado, a deposit of vanadiferous sandstone associated with carnotite was recently discovered at a place 11 miles from Rifle Creek. Three months' development disclosed 3,000 tons of 4% (V_2O_5) ore. It was estimated that in the succeeding 12 months 10,000 tons of ore, containing 400 tons of vanadic oxide, would be produced [95].

Volborthite and other vanadium minerals have been found associated with silver ores in the Silver Reef district, Washington Co., South-Western Utah [66].

A small amount of carnotite and tyuyamunite has been found associated with copper in Red Creek Canyon, Browns Park, Uinta Mts., Utah. The mode of occurrence of the carnotite seems to be similar to that of the copper minerals [67/pp. 115, 605].

Pennsylvania.—The occurrence of carnotite near Mauch Chunk, Carbon Co., Pennsylvania, has been described by Edgar T. Wherry [72], [73]. The carnotite appears as a prominent yellow stain, but irregularly distributed, on a rock wall or shelf which has been cut into the mountain-side for an electric railroad line. The carnotite occurs in a 40-ft. layer of coarse-grained conglomerate lying near the base of the Pottsville formation (Pennsylvanian), and just above the Red Mauch Chunk shale (Mississippian). The cement of the conglomerate is in most places silica, the rock being a very hard quartzite, but here and there calcite takes the place of quartz. In the quartzite, carnotite fills cracks in the pebbles themselves, and spreads over some of the slickensided surfaces, but the greater portion of the carnotite appears as a replacement of calcareous cement. The bodies formed by replacement are extremely irregular in size and shape. The mineral has been formed as a precipitate from ground water, and can be seen in process of formation where water trickles out through cracks in the rocks. Uranium-bearing minerals are common in pegmatites and vanadium-bearing dark silicates in gneisses throughout the pre-Cambrian and early Palæozoic crystalline rocks surrounding this area; and, the climate having been most probably a dry one, owing to disintegration being in excess of decomposition, there has been mechanical transportation, and subsequent concentration, of the heavy mineral carnotite.

New Mexico.—Vanadate ores occur in the State of New Mexico, as well as in *Arizona, Nevada, California* and *Michigan,* but only in the first two are they of any

importance. In these states silver-lead and copper ores, many of which contain some vanadium, have a wide distribution. The vanadium minerals are all found in the oxidized parts of the veins, and the occurrences are thus described generally by F. L. Hess [74]:

" The lead is usually accompanied by a number of other sulphides, particularly those of zinc and copper. Phosphorus and arsenic also generally accompany the veins so that, in the oxidized portions, not only lead vanadate (vanadinite) but vanadates of copper and zinc are also present. These are not present as separate minerals, but take the form of a combined vanadate of lead and zinc, or of lead, zinc and copper, and the proportion of the metals may vary considerably. The minerals may vary also by containing in whole or in part either phosphorus or arsenic in place of vanadium. Nearly all deposits contain wulfenite, the lead molybdate, and most of them contain a small quantity of tungsten. This probably does not occur as the lead tungstate (stolzite), but seems to be a component of the wulfenite. Stolzite may occur, but it is not at all common, and has rarely been recognized. The percentage of tungsten rarely, if ever, exceeds 2%. The deposits are generally small, so that no single one now known is large enough to furnish ore for a plant of considerable size.

" The deposits have been worked chiefly for their lead and silver content, and only in very exceptional cases have they served as ores of vanadium, for even when the last-named metal is present in considerable quantity, the ore-dressing and metallurgy present very great difficulties."

The localities from which vanadium ores have been reported in New Mexico are near Cutter and Cook's Peak in the Caballos Mts. [75], and at Percha Creek [76/p. 275], near Hillsboro in Sierra Co., near Magdalena in Socorro Co., and near Georgetown and Bayard in Grant Co. [68]. These deposits have never yielded any considerable quantity of vanadium. Some of them were exploited about the

years 1910 and 1911, but the mines were soon closed down and remained inoperative till the latter part of the war, when active development went on for some time, only to cease with the signing of the Armistice.

Information concerning both these deposits and those in Arizona and also New Mexico is scarce, and the only two of all in the above-named regions of which any adequate description is available are those at Palomas Gap, near Cutter, and the Lucky Bill mine near Bayard, both in New Mexico. These, however, seem to indicate the general mode of occurrence of vanadium ores in this region and must suffice.

The Palomas Gap is a pass over the Sierra de Los Caballos, a small range situated to the east of the Rio Grande, in Sierra Co. In the vicinity of Palomas Gap, the range is from 4 to 6 miles wide and the average elevation is about 6,500 ft. The Gap is about 7 miles from the north end, and about 12 miles west of Cutter, a station on the Atcheson, Topeka and Santa Fé Railway.

According to F. C. Schrader [76/p. 284], the range is mainly composed of limestone with some intercalated shale of Carboniferous age, with quartzite 50 to 200 ft. thick at the base, which is probably of Cambrian age. The quartzite rests upon what appears to be older granite. There is intrusive diorite in this granite, and in one place a poor porphyritic dyke cuts both granite and quartzite. The mines were discovered in 1906.

The principal metalliferous veins are of fissure type and are in the limestone. They extend for a distance of about two miles north and south of Palomas Gap on both slopes of the mountains with a general strike from N.E. (magnetic) to S.W., and dipping N.W. 60° to 90°. The contained metals vary considerably, for on the east side of the range the veins carry principally lead ores, while on the west copper is the important metal. Also, to the north of the Gap vanadates accompany the lead ores, and to the south molybdates, while directly opposite the pass both are present together.

Two or more veins have been worked along several ore-shoots, all of which dip to the east. The most important shoots are the Red Top, Swan and Dewey and the Benjamin, with their extensions. The primary vein-filling consists of brecciated country rock, cemented by calcite with some barytes, amethystine fluorspar, and less quartz and galena, with some cerussite, copper carbonates and vanadium minerals. The ore-shoots extend for 20 to 200 ft. along the vein and vary from mere stringers up to 20 ft. in width. The vanadium minerals comprise vanadinite, zinc-bearing cupro-descloizite, and another mineral, which may be an amorphous form of cupro-descloizite. Pyromorphite and wulfenite have also been reported to occur here [77/p. 158].

The vanadinite is found at about water-level, either as a skin of very small crystals with a velvety appearance, lining cavities known as water courses, or as a soft spongy mass of vanadinite crystals and gangue minerals, mostly calcite, known to the miners as " sand carbonates."

On the Red Top Vein, which has been traced along the outcrop for 1,500 ft., the ore-shoot was reached by shafts from 60 to 100 ft. deep. The ore consists of large pockets of " sand carbonates " from 15 to 20 ft. thick, and several carloads of ore averaging 2 to 4% vanadium were extracted. On the Swan and Dewey claims shafts 400 ft. deep had been sunk, and the ore-shoots were being followed down the dip under the Benjamin claim. The ore reserves in these shoots were said to be 20,000 tons, with an average content of 1% vanadium and 4% lead.

In 1910 the Vanadium Mines Co. put up a 75-ton concentrating mill close to the mine, and at Cutter a plant for converting the concentrate to lead sulphate and vanadic oxide, the vanadium compound being shipped to Rankin, Pennsylvania, for reduction to ferro-vanadium. The ore is soft and brittle, but the recovery from the mill was said to be as high as 75%. The plant, however, was not in operation long, and the mine was soon shut down. It reopened, though, for a short time during the war, when

the concentrating process was modified. With the signing of the Armistice the undertaking, in company with many others, was closed down again [75], [78].

According to C. H. Gordon [76/p. 275], the ores at Rio Percha consist of wulfenite and vanadinite (endlichite), together with cerussite, and lie in lenses distributed along the contact of the Mimbres limestone (Silurian or possibly Cambrian) with the overlying Percha shale (Devonian). Associated with the ores is a considerable amount of manganese, more or less quartz, and, locally, melanotekite, a silicate of lead and manganese. These mines have furnished most of the fine crystals of vanadium minerals for which Hillsboro is noted. The deposits are of moderate extent, and little or nothing was being done on them when they were examined by Gordon in 1905. It is stated elsewhere [79] that the Vanadium Queen Mining Co. of Hillsboro worked 20 claims and erected a reduction plant here in 1910, but no details are given as regards output.

The Lucky Bill lead-vanadium mine [78] is one mile from Bayard, a station on the Santa Rita Branch of the Santa Fé Railway. The country rocks here are rhyolite and tuff, resting on a quartz-monzonite porphyry. The deposit is a lode formation associated with a fault-fissure. In the porphyry there is a definite vein in the fissure, accompanied by numerous quartz veinlets highly impregnated with lead vanadate, and in the tuff above there is a band of stockwork, with lead carbonate and vanadate permeating the rocks and filling cracks. The gangue is entirely quartz, and, though some galena is present, the ore minerals are almost entirely lead vanadate and carbonate; the last two are quite clearly segregated, and can be mined separately or be separated by hand-picking. The extension of the lode of the Lucky Bill mine has been traced for several miles in both directions. In the mine the ore-shoot is 600 ft. in length and from 8 to 15 ft. wide, of which 2 to 12 ft. is shipping ore. The tenor of the ore varies between 15 and 25% lead, 18% being the lowest figure for workable ore. The vanadium content is not definitely

known, but the slags from the lead smelting are said to contain up to 16% vanadium. The vanadium ore was originally thrown on the dump as " lead oxide " or " yellow carbonates," and none has ever been shipped.

Arizona.—The occurrences of vanadium ore in this state are very numerous, but none of them seems to be of great commercial value, though vanadium ores have been shipped from some of them, particularly in the latter years of the war. The following are a few of the localities [80]: *Cochise County*: The Shattuck Arizona Copper Co.'s mine at Bisbee, near Globe, and three other places. *Coconino County*: Cataract Canyon, 45 miles N.W. of Grand Canyon station. *Gila County*: The C. and B. Vanadium mine and nine others. *Maricopa County*: The Vulture mine and four others. *Mohave County*: Missouri Mohave mine and three others. *Pinal County*: Mammoth and Old Mowhawk mines; the U.S. Vanadium Company's mine, near Kelvin, and seven others. *Pima County*: Old Yuma mine; Shamrock claim and Orizola claims near Casa Grande; and the Grand Central mines. *Yavapai County*: Silver Bell; Crown King, and five other places. *Yuma County*: The Castle Dome; Hamburg and two other places.

Of these only the United States Vanadium Co.'s Kelvin mine, the C. and B. Vanadium mine and some of the Casa Grande claims seem to have produced any quantity of ore, though the prospects at Cataract Canyon are said to be good, and a considerable amount of ore was proved in the Shattuck Arizona Copper Co.'s mine at Bisbee.

At the mine at Kelvin a 50-ton concentrating plant, using the Bryan process, was erected during the later period of the war. Here the ore is vanadinite, occurring principally along a shear zone in granite. The ore is found usually as a number of narrow seams which occasionally widen and coalesce to give an ore-body of considerable size. The vanadinite is associated with some wulfenite, and the ore is said to contain 3 to 5% vanadic oxide. Difficulties in treatment, however, led to the abandoning of the work.

Vanadium ores occur in Cataract Canyon a mile or two below the Indian village of Supai along joint planes in and as replacement of Redwall limestone. The vanadium ore takes the form of dark brown to nearly black globular aggregates lining fissures or vugs, or imbedded in the gangue. It is associated with other oxidized lead ores, together with a little zinc, but no molybdenum is present. The deposit is being developed at present to ascertain how much ore is available. The C. and B. Vanadium mine, which is the only mine in Arizona that has actually produced vanadium concentrate is in the Dripping Springs Mining district, 10 miles N.W. of Christmas, the nearest shipping point. The rocks of the district are limestone, dolerite, diorite and andesite, and are traversed by a north and south fault-zone, which is cut by numerous cross-breaks. The ores occur on a limestone-dolerite contact along the cross-breaks and minor faults. The ore-body is 25 ft. wide and 50 ft. long, and has been opened up by a series of shallow shafts and tunnels. The minerals are chiefly vanadinite, though some descloizite is found. Five hundred tons of ore are believed to have averaged between 1 and 3% vanadic oxide, and to have yielded 49 tons of vanadinite concentrate, carrying 9·5% vanadic oxide [81], [82].

Some of the deposits contain rather large quantities of wulfenite, as at the Mammoth and at the neighbouring Mowhawk mine ; in these the ore contains wulfenite, vanadinite, descloizite, cerussite, anglesite, chrysocolla, azurite and malachite, with a little galena here and there. At the Shattuck Arizona Copper Co.'s mine, Bisbee, vanadinite occurs in a large vug deposited on brecciated quartz and is difficult to mine. At one time (1915) vanadium-bearing ore was exposed on the 600 ft. level for a length of 200 ft., with an average width of 3 ft. The vertical height of the ore-shoot was about 600 ft., and the estimated reserve of ore with 10% vanadic oxide was 3,000 tons, in addition to a large tonnage of low-grade (1 to 1·5% V_2O_5) ore. The vanadium mineral is mainly cupro-descloizite, and occurs in the form of stalactites in radial aggregates from

half a millimetre to several centimetres in diameter. The larger forms are coated with a red powder, but the smaller aggregates are olive-coloured, with a dark olive streak; the red powder also occurs in a layer between the cupro-descloizite and the quartz. This ore was tested as a source of vanadium during the war, and a process was worked out for the recovery of the metals; however, little further work has been done.

Michigan.—About 7 miles north of Skanee, Baraga Co., Michigan, endlichite (a lead vanadate) occurs in a nearly vertical fissure-vein in altered serpentine, striking N.E. to S.W. and 24 in. in thickness at a depth of 12 to 13 ft. The foot-wall is slate. An analysis of this ore showed 21·5% vanadium, with traces of uranium [83].

Oregon.—A deposit of carnotite has been reported in Eastern Oregon. A sample contained 7% vanadic oxide, and 9% uranium oxide [48].

Vanadate ores have also been reported from the Sangre de Cristo Range, Huerfano Co., *Colorado* [59/p. 52]. Near Klinefelter [59/p. 54] on the main Santa Fé Railway, and Camp Signal [84], in San Benardino Co., *California*, and Good Springs, *Nevada* [85], and several other places in the United States. From Good Springs a little psittacinite or mottramite was shipped towards the end of the war, and a number of deposits of descloizite have been exploited in the same district.

Asphaltites in the United States

Through the Washita Mt. district of Oklahoma and Arkansas are large deposits of asphaltite of the grahamite type. Material from the outcrop near Page yielded, after burning, 0·85% ash, which contained 14% vanadium. The veins are enclosed in highly tilted form or folds, and range from 10 to 28 ft. in thickness. The asphaltite has been crushed after its intrusion into the faults enveloping it. At Mena, Arkansas, the asphaltite gave 0·65% ash, with 15% vanadium. Near Palaisade, Nevada, a vein of asphaltite,

with highly faulted strata, occurs from a few inches to 3 ft. in thickness. An average sample yielded about 4 lb. metallic vanadium per ton.

SOUTH AMERICA

Vanadium ores are found in Argentina, Chile and Peru, but only those of the last country are of great importance.

ARGENTINA

The country of Argentina is responsible for a very small output of vanadium ores, and the occurrences are more of theoretical interest than of commercial value. The metal has been reported from two areas: The western slopes of the Andes, in the Province of Mendoza, and in the provinces of San Luis and Córdoba. The deposits of the two last-named provinces have a wide distribution, and are of normal type, being vanadate ores associated with the oxidized portions of lead lodes. Only one or two of the deposits, however, are of any value, and these are not very important, since the vanadium content soon falls off in depth, and, what is more, many of the mines, which have been operated for lead, have been abandoned. In the Guaico district of the Province of Córdoba the ores are found in the oxidized parts of E.–W. silver-lead veins, and have been mined at the Venus, Rara Fortuna and Bien Venida mines. These mines were famous for their silver output, but in 1910 were abandoned, owing to the flooding of the workings. The ores are vanadinite, descloizite and brackebuschite [86/p. 48]. Vanadium ores with a content of 10% vanadium have also been worked at Cruz del Eje in this province [6/p. 725]. These ores, however, disappeared in depth, leaving galena only. Bodenbender refers to the wide distribution of vanadate ores in the province of San Luis [87]. In two localities examined by him occur lead and bismuth lodes respectively. The lead lode is vertical, has a width at surface of about 6 ft., and cuts phyllites. The vein has

brecciated walls, and is filled for the most part with quartz gangue, which changes to carbonates in the centre of the vein. Galena occurs as lenses, composed of nodular masses, which are partly altered on the external surfaces, and generally have an unaltered core. The vanadium minerals are found lining cavities in a band of compact or cavernous granular gossan, containing quartz and calcite with lead carbonate and limonite, in addition to some iron silicate and a small amount of molybdates, such as wulfenite and phosphates. The vanadium is partly present as vanadinite, but in part contributes to the formation of a complex yellow-green mineral, containing vanadium, phosphorus, lead, copper and iron, which occurs as incrustations on a clear blue homogeneous mineral in bands of copper silicate and molybdate. The origin of the vanadium is, as is usually the case with such deposits, uncertain. The vanadinite is very frequently associated with wulfenite, and appears to grow from it, as though formed by the action of vanadic acid on the molybdate. There is, however, no vanadic acid to be found in the unaltered wulfenite.

The petroliferous region of Mendoza and Neuquén is characterized by the occurrence of deposits of asphaltite, in the form of rafaelite (albertite). At Auca Mahuida in Neuquén, a vein of rafaelite occurs in Upper Cretaceous sandstones and arenaceous marls, striking W.N.W., from 3 to 10 ft. in thickness and traceable for about 5 miles in length. The wall is bleached and has a narrow selvage containing 2·7% copper. Between this and the hard resinous rafaelite there is, in places, a band of gypsum. An analysis of the rafaelite showed the following percentages: Volatile matter, 57 to 66; fixed carbon, 34 to 43; ash, 0·3 to 0·6; sulphur, 3 to 5; nitrogen, 1 to 1·2; calorific value, 9,000 to 10,000 B.T.U. The ash consists almost entirely of vanadium salts. At Los Buitres rafaelite occurs along the contact of mica-diorite and variegated argillaceous sandstones and in fractures in the mica-diorite close to the contact [86/p. 52].

Vanadium has been reported to be present in petroleum

residues in Argentina [88]. The output of vanadium ores in Argentina has been entirely derived from the Córdoba deposits. The amounts are somewhat uncertain, but for the years 1911 and 1912 they were 14 and 40 metric tons respectively.

Chile

Vanadium minerals have been reported from several places in the Province of Coquimbo, Chile, between 150 and 200 miles north of Valparaiso. They all belong to the vanadate class of ores, and are associated with silver-lead and copper deposits. The most important deposits are those of the silver mines of Arqueros in the Department of La Serena [86/p. 283], and in the copper mines of Talcuna [6/p. 726], about 3½ miles north of Marqueza. Here the vanadium deposit takes the form of a yellow earth with 6% vanadium in veins of copper ore. Extraction of the metal was begun in 1900, but the vanadium gave out at a depth of 65 ft. The vanadium was associated with barytes and a little copper. Vanadinite is reported from the Mina Grande near Marqueza, where it is found in the outcrop of a vein carrying lead and copper ores.

Peru

The vanadium deposits of Peru are in the departments of Junín and Lima, and, as already mentioned, comprise the patronite of Minasragra, and a number of veins of asphaltite, the so-called "coal veins of Peru." They are all in the western chain of the Andes, at no great distance from the watershed, and at elevations ranging from 12,000 to 16,000 ft. Along the watershed and towards the S.W. the country is composed of folded Jura-Trias and Cretaceous rocks, while to the N.W. more recent intrusive rocks are found. The intrusive rocks are said to be, for the most part, monzonites, and to be also the parent source of the valuable metalliferous deposits of the Department of Junín. The Jura-Trias sediments are chiefly sandstones and con-

glomerates, while the Cretaceous rocks are grey and green shales and limestones, the latter being very thick and massive, and forming the highest ridges of the mountains.

The asphaltite veins [89], [90] occur in four districts—Yantac, Sillapata, Huari and Yauli. They are confined to sedimentary rocks, principally limestone, and occasionally shale or sandstone, and are found as fissure veins cutting obliquely across the bedding, and occasionally forming flats or *mantos* along the bedding-planes. The veins form a series of lenses, placed end to end, and vary from a few inches to 40 ft. in width, the wide deposits being known as *bolsonados*. Some of the veins are traceable for about 13 miles. As a rule the veins swell out in the limestone and pinch to a series of stringers in the shale, but at the Negrita mine, Yauli district, a vein, 2 ft. thick, is entirely enclosed by, and has been traced for some distance in, shale. The asphaltite breaks cleanly from the walls, especially when these are of limestone, but sometimes the country rock on either side is impregnated with films of asphaltite. Two types of asphaltite occur in Peru: One allied to grahamite, found at Huari, which is bituminous, burning with a long yellow flame and melting easily to a sticky tar-like mass, and the other allied to impsonite, occurring in the other three districts, which is anthracitic, being lower in volatile matter and higher in fixed carbon than the former. The ash content of the Peruvian asphaltites varies from 1 to 47%, but is usually low, while that of the vanadium in the ash varies from 0·9 to 15%, the average being 4 or 5%. When the asphaltites are burnt there is incomplete combustion, the ash always retaining some undecomposed hydrocarbon.

In considering the genesis of the deposits, Baragwanath [90] supposes that certain fissures at one time tapped "pools" or reservoirs of heavy asphaltic petroleum existing in the limestones or shales or in some underlying formation. The oil probably arose in the fissures through hydrostatic pressure. The asphaltites were then formed by the inspissation of the petroleum. The vanadium was probably

an original constituent of the petroleum itself. In this connection it is of interest to know that some years ago an oil-pool was found in West Virginia, by drilling on one side of a vein of grahamite [91]. Vanadium has been found in the petroleum residues of Argentina (*see* p. 55), and possibly occurs in other petroleums, especially those which are largely of vegetable origin. It has also been found in the ash of rafaelite occurring in the petroliferous region of Mendoza and Neuquén, Argentina (*see* p. 55).

The Peruvian asphaltite has been used locally on a small scale for domestic fuel and for furnishing asphalt for paving purposes, and, on a large scale, for supplying smelting works, *e.g.* a blast furnace coke has been made from a mixture of the bituminous and anthracitic varieties. Several attempts have been made to extract the vanadium on a commercial scale, but hitherto without success.

The Yantac and Sillapata deposits (altitude 14,000 to 16,000 ft.) are situated along a line ranging about N.N.W. to S.S.E., 60 miles east of Lima. They consist of anthracitic asphaltite in Cretaceous limestone, but are too small, irregular and friable to be used as fuel. The asphaltite averages 7% and less than 1% vanadic oxide in Yantac and Sillapata respectively. The Huari and Yauli deposits are along a line parallel with, and 40 miles to the east of, the last. In the Yauli district, the asphaltite is mined for fuel, particularly at the Rumichana mine. It is anthracitic, and is separable into clean asphaltite, low in ash and " bone," an impure asphaltite of high ash content. The hydrocarbon burns with little or no flame, and leaves a light feathery ash, which turns green on exposure to air, owing to the presence of vanadium, the content of which is high, and these mines are of interest as a potential source of the metal. At the Rumichana mine the vein strikes N. 37° W., dips between 70° and 90°, and varies from a few inches to 40 ft. in thickness. The asphaltite is friable and low in ash. The run of mine material gave 16% ash containing 5·3% vanadic oxide; the clean screened asphaltite averaged 9% ash, containing 7% vanadic oxide. At Llacsacocha the

material will probably yield 4 to 5% ash, containing between 15 and 20% vanadic oxide, and the Negrita material appears to be similar. These mines have produced considerable quantities of asphaltite, 2,000 metric tons having been obtained from the Negrita deposit alone.

The grahamite type of asphaltite occurs in the neighbourhood of Huari, that is in the region around Oroya, Huari, Chacapalpa and Llocllapampa and the *haciendas* of Cochas, Pachacayo and Cachi-Cachi. The asphaltite occurs in nearly vertical fractures and fissures in bituminous limestones of Lower Cretaceous age. The principal vein, known as La Lucha, strikes N.E.–S.W. in bituminous limestone, having a few argillaceous layers, and a general trend of N.W.–S.E., the dip being N.E. or S.W. The asphaltite varies in thickness from 3¼ to 11½ ft. The filling has suffered a compression, which has produced joints therein, which strike E.–W. Analyses of samples from La Lucha gave the following percentages: Volatile material, 36 to 57·47; fixed carbon, 39·29 to 45·57; ash, 1·35 to 10. The ash contained: Silica, 10·62; peroxide of iron, 5·54; vanadic oxide, 44·05; lime, 23·39; sulphur, traces; undetermined (CO_2, etc.), 16·40 [92]. The asphaltite has been mined as fuel at La Lucha as well as at Chuichos.

The asphaltite of the Huari district has usually a low ash content which varies between 2·2 and 5·7%, and which contains from 1 to 2·5% vanadic oxide, so that few of the veins can be considered seriously as sources of the metal.

The vanadium in the Peruvian asphaltites probably occurs as a sulphide (patronite).

The most important vanadium deposit in the world is that at Quisque (Minasragra), Province of Pasco, Department of Junín. For a long time the deposit was supposed to be coal, but in 1905, Antonio Rizo Patron discovered that it contained a large percentage of vanadium, whereupon he and E. E. Fernandini obtained possession of the claims and subsequently sold them to the American Vanadium Co. Later, they passed into the hands of the Vanadium

Corporation of America. The mineral was found to be a sulphide of vanadium, and was named patronite after the discoverer. Since it has been mined the Minasragra deposit has contributed about 80% of the world's production of vanadium.

The Minasragra mine [86], [89], [93] lies about 30 miles N.N.W. of Yauli, at an altitude of 16,500 ft. The deposit is on the eastern slope of the main or coastal Cordillera of the Andes, between two ranges, trending N.N.W.–S.S.E., formed of Mesozoic limestone. The area between these two ranges is built up of red and green shales, also of Mesozoic age. The vanadium deposit is confined to red gypsiferous shales in the upper part of the series, whilst the lower portion of it is characterized by layers of limestone. In the region are numerous dykes and masses of igneous rocks ranging from quartz-porphyry to dolerite in composition. The deposit is a lens-shaped mass about 300 ft. in length, with a maximum width of 30 ft. The strike is N. 20° W., or parallel to, and the dip is 75° or steeper than, the enclosing shales. The deposit is principally made up of the following minerals, placed in order of abundance: *Quisqueite,* a black lustrous hydrocarbon; *coke,* a dull black vesicular hydrocarbon, and *patronite.* The vanadium ore contains minute amounts of a reddish-yellow mineral, a nickeliferous sulphide of iron having the formula (Fe,Ni)S, named bravoite by Hillebrand, as well as an undetermined silicate resembling halloysite.

Typical analyses of the three principal constituents are given in the table on opposite page.

Small amounts of ferric oxide, manganese, chromic oxide and alumina are also present.

The purest patronite yields between 19·3 and 24·8% vanadium, and the formula is generally stated to be $V_2S_5 + 4S$.

Oxidation has taken place to a considerable extent in the upper portion of the deposit; for instance, close to the surface, there are red and brown vanadates, which, at the depth of a few feet, give way to a greenish-black

—	Patronite.	Quisqueite.	Coke.
Sulphur (soluble in carbon bisulphide)	4·50	15·44	0·64
Sulphur (combined)	54·29	31·17	5·36
Carbon	3·47	42·81	86·63
Hydrogen	—	0·91	0·25
Nitrogen	—	0·47	0·51
Oxygen (by difference)	—	5·39	4·64
Water (at 105° C.)	1·90	3·01	—
Ash	—	0·80	1·97
Vanadium	19·53	—	—
Iron	2·92	—	—
Nickel	1·87	—	—
Silica	6·88	—	—
Titanic oxide	1·53	—	—
Phosphoric oxide	2·00	—	—

calcium vanadate. The calcium vanadates, hewettite, metahewettite, pascoite, fernandinite, and the vanadium sulphate, minasragrite, are among the alteration products, which have been identified and described. These oxidized compounds may replace the shale country almost entirely, or merely fill cracks in the crushed zone. The oxidized zone has a considerable width, and extends downward to a depth between 100 and 200 ft., or to the lower limit of percolating water. It is a direct result of the rainless character of the region, for were there any considerable precipitation, the oxidized zone would be rapidly dissolved and removed. As a matter of fact, the water flowing from the mine contains a noticeable amount of vanadium in solution, and a plant has now been installed to recover the metal from the mine waters, which will result in a saving estimated at $500,000 (U.S.) per annum.

According to Hewett [89], "brown oxide" contains 72·50, "red oxide," 67·60, and "green oxide," 57·33% vanadic oxide. The green oxide contains in addition 4·76% hypo-vanadic acid (V_2O_4). Molybdic oxide was present in the red and green oxides to the extent of 2·82 and 3·28% respectively. The green oxide contained a large proportion of ferric oxide.

Hewett gives a cross-section of the deposit near the surface. From this it appears that the quisqueite occurs

on both walls. On the hanging-wall side, next to the quisqueite, is a thin band of patronite. Then comes a band of coke, having a clay vein in its centre. A second layer of patronite, much thicker than the other, forms the middle portion of the deposit, and, finally, there is a second band of coke between the patronite and the quisqueite lying on the foot-wall side. A quartz-porphyry dyke is seen to cut across the shales. According to Miller and Singewald [86/p. 490], this dyke is probably more recent than the patronite deposit, as the ore in direct contact with the intrusive rock appears to have been baked or metamorphosed by it. They regard the deposit as having been formed by a replacement of the shales along a zone of crushing, and show that the shales originally contained beds of gypsum, as well as a network of narrow gypsum stringers, and that both beds and stringers have been removed in a large part of the main mass of the ore. On the other hand Hewett regards the deposit as an extreme phase of differentiation of asphaltite under the stimulus of the igneous intrusion, and he is of opinion that the dyke is older than the vanadium deposit. Explorations made since 1907 [86/p. 491] show that the central lens of patronite, coke and quisqueite is entirely enclosed by a zone of material, locally called *veta madre*, which is 40 ft. thick on both walls of the smaller lens, and extends beyond its ends. Veta madre is a mixture of earthy material, disseminated patronite (with 1 to 12% vanadium) and anhydrite, which is largely altered to gypsum on the level of tunnel No. 2, 120 ft. below the surface. According to Hewett, it represents shale that has been more or less saturated with sulphide of vanadium and replaced by the anhydrite.

When the mine was first opened, only oxidized ores yielding an average of 20% vanadic oxide were worked, but at present only unaltered sulphides, or mixed sulphides and oxides, are extracted. These ores, after roasting in reverberatory furnaces, have yielded from 18 to 50% vanadic oxide. In recent years the grade of concentrate exported has fallen considerably, the richest ore having

been worked out, and early in 1921 the company was projecting a 20,000 kilowatt hydro-electric plant on the Jumasha River, and a new treatment plant at Jumasha to produce a concentrate carrying between 80 and 90% vanadic oxide.

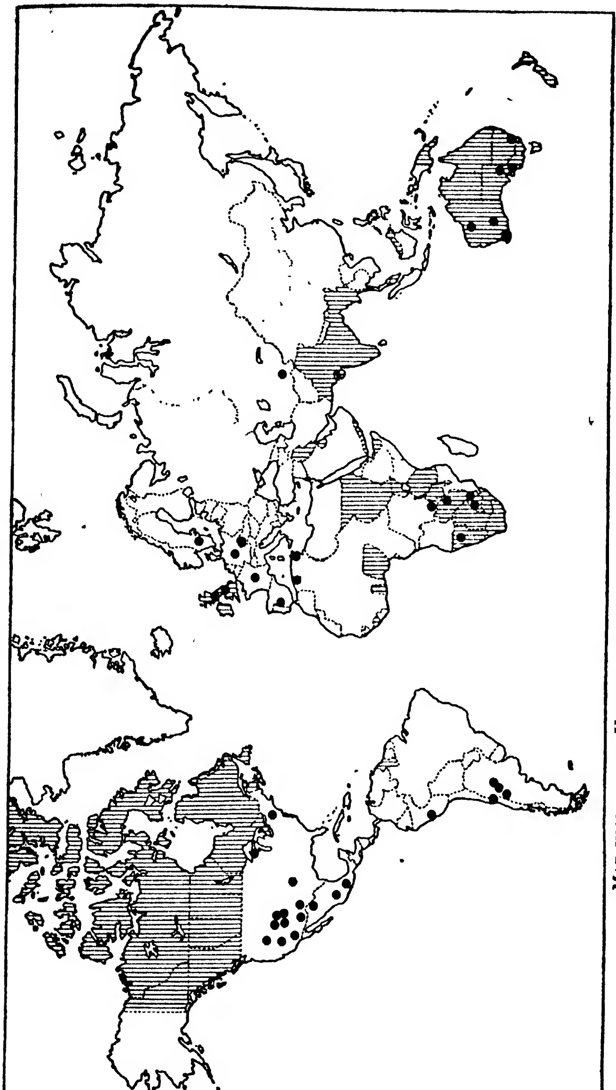
Originally the mine workings consisted of a large open cut in the oxidized ore, but the deposit is now being opened up by adits, the lowest of which intersects the vein 120 ft. below the surface. The ore was formerly transported by llamas, except for 9 miles across the intervening Lake Punrún, where barges were used; but within the last few years, a narrow-gauge railway has been built from the mine to the lake, a distance of 6 miles, and a 16-mile motor-road has been constructed from the east shore of the lake to Ricrán, on the Cerro de Pasco Railway. This road will shortly be supplemented by a narrow-gauge railway. The concentrate is ultimately shipped to the company's smelting works at Bridgewalls, Pennsylvania, for reduction to ferro-vanadium.

The ore in sight (or blocked out) is estimated to contain 16,500 metric tons of vanadium (metal). The total reserves are put at 45,000 tons of metal. In 1919 the Vanadium Corporation of America, owning Minasragra, bought up the Primos Chemical Co., thereby acquiring extensive holdings in the Colorado roscoelite deposits, and has also acquired an option of purchase on the Llacsacocha asphaltite mines in the Yauli district, Peru [94]. It is stated that recent extension of adits and of diamond drilling has revealed the presence of another large body of vanadium ore at Minasragra of the same character and richness as the original body now being worked.

Exploitation at Minasragra began in 1907; from 1907 to 1919, inclusive, a total of 27,998 metric tons of ore was raised, containing 10,413 metric tons of vanadic oxide [7/No. 100, 1921]. The whole of the Peruvian output of vanadium ore at present comes from Minasragra. The individual productions from 1909 to 1921, inclusive, are given in the table on page 14.

Owing to the large stocks of ore on hand and to the poor market, the mine was not worked in 1922.

In January 1921 the export tax on vanadium in Peru was changed to £4·529 per metric ton of ore or concentrate, irrespective of vanadic oxide content or price [94].



Map showing the Vanadium-bearing Districts referred to in the Text
(British Empire shaded)

REFERENCES TO LITERATURE ON VANADIUM

A.—Publications referred to by Numerals in the Text

General

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